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REM IV

Remedial Planning Activities
at Selected Uncontrolled
Hazardous Waste Sites–Zone II

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ICF
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ASSESSMENT OF THE TOXICITY OF COPPER, MERCURY, SELENIUM, SILVER AND THALLIUM IN SOIL AND PLANTS IN THE HELENA VALLEY OF MONTANA

for

EAST HELENA SITE (ASARCO)
EAST HELENA, MONTANA

EPA Work Assignment No. 68-8L30.0

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Glossary of Units, Symbols, and Acronyms

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Units

kg	kilogram; kg = 10^{3} g
g	gram = 10^{-3} kg
mg	milligram; mg = 10^{-3} g
ug	microgram; ug = 10^{-3} mg
ng	nanogram; ng = 10^{-3} ug
L	liter; L = 1 dm^{3}
ml	milliliter; ml = 10^{-3} L

Symbols

ppm	parts per million = ug/g = mg/kg
ppb	parts per billion = 10^{-3} ppm, ng/g = ug/kg
ug/g	microgram/gram
mg/kg	milligram/kilogram
mg/L	milligram/liter
ug/L	microgram/liter
ug/ml	microgram/milliliter
ng/ml	nanogram/milliliter

Acronyms

AAS	Atomic absorption spectrophotometry
AOAC	Association of Official Agricultural Chemists
AWT	Ash weight basis
CCM	Copper carbonate method
CEC	Cation exchange capacity
DTPA	Diethylenetriaminepentaacetic acid
DW	Dry weight basis
EDTA	Ethylenediaminetetraacetic acid
EPA	Environmental Protection Agency
EPA CV	Environmental Protection Agency cold vapor method
ES	Emission spectrographic
FLAAS	Flameless atomic absorption spectrophotometry
GLC	Gas liquid chromatography
INAA	Instrumental neutron activation analysis
IPAA	Instrumental photon activation analysis
MMC	Methyl mercuric chloride
MMH	Methyl mercuric hydroxide
MYC	Mycorrhiza
ND	Not determined
NOAA	National Oceanic and Atmospheric Administration
NR	Not reported
NRC	National Research Council
OM	Organic matter content
pH	Negative logarithm, base 10, of H^{+} concentration
PMA	Phenyl mercuric acetate
RNAA	Radiochemical neutron activation analysis
SSMS	Spark source mass spectrometry
USDA	United States Department of Agriculture
USGS	United States Geological Survey
WW	Wet weight basis
XRFL	X-ray fluorescence
YR	Yield reduction

1.Ø INTRODUCTION

This document consists of a literature review and presents candidate levels of copper, mercury, selenium, silver and thallium for assessment of selected environmental hazards associated with the East Helena smelter located in the Helena Valley of Montana. This document is the second of two volumes. Volume one contains similar hazard levels for arsenic, cadmium, lead and zinc in addition to an evaluation of the hazard to livestock from these four elements. Candidate hazard levels presented in this report have been developed specifically for the East Helena, Montana smelter site. The use of this document for evaluation of other sites should be attempted only with proper consideration of site specific conditions.

1.1 Purpose

This document is a literature review from which proposed hazard levels have been developed to assess risk from chemical element levels found in soils and crops present in the vicinity of the East Helena smelter. These hazard levels will enable determination of the potential danger to these agricultural resources.

1.2 Scope

The scope of this document is confined to the metals copper, mercury, selenium, silver and thallium and their toxic effects and levels of accumulation in soils and plants. This document does not contain a review of relevant literature pertaining to extractable levels of these metals in soils.

1.3 Methods

Portions of the literature that are presented in this document were procured through the use of a computer search utilizing numerous data bases including AGRICOLA, BIOSIS, CAB Abstracts, CRIS-USDA, ENVIROLINE, MEDLINE, NTIS, Pollution Abstracts, SCISEARCH and Water Resources Abstracts. Conventional

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library methods have also been employed for researching abstracts, periodicals and other materials. The authors are cognizant of the limitations of solution culture and greenhouse studies but for some aspects of the five metals reviewed, these are the only data available.

Background values presented were taken directly from the scientific literature. Phytotoxic levels were chosen through; 1) a review of levels reported to be phytotoxic in experimental studies and 2) a comparison of the reported experimental results with phytotoxic levels established by others. The scarcity of data precluded establishment of an upper tolerable concentration for some of these elements. Scientific literature that most closely approximated conditions present in the Helena Valley were emphasized more for hazard level selection. For example, a toxic soil level for wheat on calcareous loamy soil was considered more applicable than a toxic soil level for cabbage on a sandy acid soil. Once hazard levels were developed they were compared to means and ranges of soil/plant elemental levels measured in the Helena Valley and control sites.

All values reported in this document are on a dry weight basis unless otherwise indicated.

1.4 Site Description

The Helena Valley is located in west central Montana and trends in a west northwest direction. It is 35.4 km (22.1 mi) long and 17.1 km (10.7 mi) wide. The valley is bounded on the northeast by the Big Belt Mountains, on the south by the Elkhorn Mountains and the Boulder Batholith, and on the west by mountains forming the continental divide. Lower portions of the valley are occupied by Lake Helena and Hauser Lake formed by Hauser dam on the Missouri River. Elevations range from 1,113 m (3650 ft) mean sea level at Hauser Lake to 2,560 m (8,400 ft) in the surrounding mountains. Geological materials on the valley floor consist of quaternary and tertiary sediments that are consolidated to poorly consolidated. Soils are moderately calcareous and composed of silt and clay (Miesch and Huffman 1969). Soil profiles are poorly to moderately developed on both quaternary and tertiary parent materials. The Helena Valley is semi-arid and receives from less than 25.4 cm (10 in) to less than 36 cm (14 in) of annual precipitation. The adjacent mountains receive up to 76.2 cm (30 in) of annual precipitation (U.S. Soil Conservation Service 1981). The climate is modified continental with an average annual temperature of 6.3°C (43.3°F) (National Oceanic and Atmospheric Administration (NOAA 1983). Average January and July temperatures at Helena are -8°C (18.1°F) and 20°C (67.9°F) respectively (NOAA 1983). Agricultural crops in the Valley are alfalfa, small grains (usually wheat, barley and some oats) and range land.

The Helena Valley is the site for two incorporated cities: Helena and East Helena with approximate populations of 23,900 and 2,400 respectively (1980 census). The two cities are located 6.4 (4 mi) and 1 km (0.6 mi) from the smelter complex, respectively.

The valley has been the site of a lead smelter since the Helena and Livingston facility was built in East Helena in 1888. The smelter was purchased by its present owner (American Smelting and Refining Company) in 1899. The Anaconda Company built a zinc plant adjacent to the smelter in 1927 to recover zinc from waste products. In 1955 the American Chemet Company constructed a paint pigment plant utilizing zinc oxide from the zinc facility.

2.0 BACKGROUND AND ELEVATED LEVELS OF COPPER, MERCURY, SELENIUM, SILVER AND THALLIUM IN SOILS AND PLANTS.

Varing amounts of research data are available for copper, mercury, selenium, silver and thallium. For copper and, to a lesser extent, mercury a large volume of work has been completed in reference to sewage sludge disposal problems. Our understanding of selenium has benefited from the studies of selenium accumulator plants and their adverse effects on livestock. Little data are available to accurately evaluate levels of silver and thallium found in soils and plants. Copper is the only one of these elements considered essential for higher plants (Kabata-Pendias and Pendias, 1984). Sections 2.1 through 2.5 discuss unique characteristics of each metal reviewed and levels found in soils and plants.

2.1 Copper Levels in Soils and Plants

Copper is one of the most studied heavy metals. Extensive literature has been published concerning the role of copper in animals and plant nutrition, sewage sludge disposal, and environmental pollution from industrial sources. Study of the beneficial and toxilogical effects of copper in agricultural crops date from research published by Grossenbacher (1916), Floyd (1917) and Forbes (1917).

The total concentration of copper in the earth crust has been reported at approximately 50 ppm (National Research Council, NRC 1977). Bowen (1966) reported copper levels in igneous rock, shale, sandstone and limestone as 55 ppm, 45 ppm, 5 ppm and 4 ppm respectively. The copper content of shale, bituminous shale, sandstone and limestone and dolomite were reported by others as 35 ppm, 70 ppm, 30 ppm and 6 ppm respectively (Wedepohl and Zemann 1974). These authors also reported a copper concentration in coal as 17 ppm. Copper is most abundant in mafic and intermediate rocks and minerals such as biotite and pyroxene (Cox 1979, Mitchell 1971, Thornton 1979). It is usually found as simple and/or complex sulfides, many of which are easily soluble, especially in acid environments (Kabata-Pendias and Pendias 1984, NRC 1977). Copper also occurs as a native metal (Cox 1979).

Haque and Subramanian (1982) reported atmospheric emissions of copper as 18,500 and 56,000 metric tonnes per year for natural and anthropogenic sources respectively. It was estimated that 65 percent of the natural emissions occur from windblown dusts and that "vegetative exudates account for the bulk of the remainder" (Nriagu 1979). Metallurgical processing and wood combustion have been reported as the major sources of anthropogenic copper at levels of 19,800 and 11,500 tonnes per year, respectively. "About 95 percent of the anthropogenic copper emissions comes from point sources such as smelters, utility plants and incinerators" (Nriagu 1979).

2.1.1 Total copper levels in soils

A complete discussion of the role and function of copper in soils and plants is beyond the scope of this document. The following brief discussion is provided to help the interpretation of reported soil levels.

The copper content of most soil is determined in part, from copper present in parent material. The soil level is modified to varying degrees by pedogenetic processes (Thornton 1979). These processes include climatic factors which determine the amount of weathering and degree of soil formation, topography, soil pH, the redox potential and the organic matter content (Baker 1974).

The form of copper in soils remains somewhat obscure. Although copper occurs in two valence states, Cu^{+1} and Cu^{+2}, copper in soil is almost exclusively in the Cu^{+2} form (Thornton 1979).

The three soil parameters most likely to control copper availability to plants are pH, cation exchange capacity (CEC) and organic matter content (OM). The soil pH is the parameter most consistently identified in the literature as controlling metal availability to plants. All microelements, with the exception of molybdenum and selenium "are more labile at low pH due to hydrolysis of hydroxide species and (increased) solubility of other solid phase minerals such as carbonates and phosphate (Logan and Chaney 1983). A pH level $\geq$6.5 is considered to be effective in reducing the plant availability of soil copper and other metals (Chaney 1973, CAST 1976). Copper is sorbed or bound more strongly to soil colloids and organic matter than are many other cations (Reuther and Labanauskas 1966, Thornton 1979). Leeper (1972) suggested that soil CEC be used as an index to determine the amount of metals that can be added to a soil without producing phytotoxicity. This index may be more applicable to smelter pollution than it is to sewage sludge due to the sorption properties of sludge which dominate the CEC and OM properties of the soil to which it is applied (Corey 1981). The humic, fulvic and tannic acids of organic matter form stable compounds with copper and other metals (Stumm and Morgan 1970). Stevenson and Ardakani (1972) have reported that copper organometallic complexes are more stable than similar complexes of lead, iron, nickel, manganese, cobalt and zinc at a pH of 5. Nickel and copper are typically associated with soils high in organic matter content (Hazlett et al. 1983).

The background total soil copper concentration can range from 1 to 300 ppm with means generally in the range of 10 to 50 ppm (Table 1). Kubota (1983) reported a range and mean of 2-137 ppm and 30 ppm respectively for Western United States valley fill materials.

Elevated copper levels in soils are less well documented than are background data (Table 2). Much of these data related to elevated copper levels in soil have been associated with sewage sludge disposal problems. The interactions of other metals with copper in sludges and the effect of sludge organic matter make interpretation of these data difficult. Elevated copper data reported in reviewed literature ranged from typical background levels to the 2254 ppm copper found in abandoned open ore roasting areas (Hogan et al. 1977). Selection of hazard levels for elevated copper concentrations in soils is presented in Section 3.1.

Table 1. Background total copper levels in soils.

Medium	Use	Level (ppm DW) Means in ()	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Minnesota Soils	Not given	16-50 (26)	Background	NR	NR	NR	Tri-Acid AAS	Field	Pierce et al. (1982)
Japanese Soil	Not given	4.4-176 (34)	Background	NR	NR	NR	Not given	Field	Kitagishi and Yamane (1981)
Organic Muck Soils	Uncultivated	2-27	Background	Plant Uptake	NR	Maturity	AAS	Field	Czuba and Hutchinson (1980)
Surface - Ontario	Truck Farm	72-213	Background	Plant Uptake	Vegetables	Maturity	AAS	Field	Czuba and Hutchinson (1980)
Organic Muck Soils 40-48 cm - Ontario	Truck Farm	1-123	Background	Plant Uptake	Vegetables	Maturity	AAS	Field	Czuba and Hutchinson (1980)
Ontario Soils	Crops	(15.9)	Background	NR	NR	NR	AAS	Field	Czuba and Hutchinson (1980)
Piedmont Soils	Forage	13-191 (52)	Background	Plant Uptake	Legumes/grasses	Not given	Dithizone/	Field	Price et al. (1955)
California Soils	Crops	8-112 (54)	Background	Plant Uptake	Legumes/grasses	Not given	Carbamate/ Colormetri- cally AAS	Field	Kubota (1983)
Western US Valley Fill	Crops	2-137 (30)	Background	Plant Uptake	Legumes/grasses	Not given	"	Field	Kubota (1983)
Glacial Drift N. Central and	Crops	1-119 (17)	Background	Plant Uptake	Legumes/grasses	Not given	"	Field	Kubota (1983)
New England	Crops	1-179 (24)	Background	Plant Uptake	Legumes/grasses	Not given	"	Field	Kubota (1983)
Alluvium (Calif)	Crops	1-55 (15)	Background	Plant Uptake	Legumes/grasses	Not given	"	Field	Kubota (1983)
Coastal Plain (SE.US), NC, SC	Crops	8-34 (19)	Background	Plant Uptake	Legumes/grasses	Not given	"	Field	Kubota (1983)
Coastal Plain Fl, NC, SC	Crops	1-13 (5)	Background	Plant Uptake	Legumes/grasses	Not given	"	Field	Kubota (1983)
Western US Soils	Native Range/ Crops	2-300 (21)	Background	Plant Uptake	Native Range/ Crop Plants	Not given	NR	Field	Shacklette and Boerngen (1984)
US Soils	Native Range/ Crops	(17)	Background	Plant Uptake	Native Range/ Crop Plants	Not given	NR	Field	Shacklette and Boerngen (1984)
Surface Soil/	Native Range	14 (Geo. Mean)	Background	Plant Uptake	Sagebrush	NA	AAS	Field	Connor et al. (1976)
Powder River Basin	Native Range	3-30 Range	Background	Plant Uptake	Sagebrush	NA	AAS	Field	Connor et al. (1976)
Subsoil/Powder	Native Range	16 (Geo. Mean)	Background	Plant Uptake	Sagebrush	NA	AAS	Field	Connor et al. (1976)
River Basin	Native Range	5-50 Range	Background	Plant Uptake	Sagebrush	NA	AAS	Field	Connor et al. (1976)
Near Sudbury Ont.	Native Plants	61-98	Background	Plant Uptake	Agrostis gigantea	Maturity	AAS	Field	Hogan et al. (1977)
Organic Soils 0-15 cm	Crops	29.5-111.0 (65.0)	Background	Plant Uptake	Crops	NR	AAS	Field	Ishida and Suda (1976)
Sandy Soils 0-15 cm	Crops	2.1-123.0 (20.2)	Background	Plant Uptake	Crops	NR	AAS	Field	Ishida and Suda (1976)
Loam Soils 0-15 cm	Crops	3.8-144.0 (25.5)	Background	Plant Uptake	Crops	NR	AAS	Field	Ishida and Suda (1976)
Clay Soils 0-15 cm	Crops	9.5-77.2 (16.7)	Background	Plant Uptake	Crops	NR	AAS	Field	Ishida and Suda (1976)
All Ontario Soils	Crops	2.1-144.0 (21.5)	Background	Plant Uptake	Crops	NR	AAS	Field	Ishida and Suda (1976)
Canadian Shield Soils	Uncultivated	(11)	Background	Plant Uptake	NR	NR	AAS	Field	McKeague and Wolynetz (1980)
Canadian Appalachian	"	(17)	Background	Plant Uptake	NR	NR	AAS	Field	McKeague and Wolynetz (1980)
St. Lawrence Lowlands	"	(19)	Background	Plant Uptake	NR	NR	AAS	Field	McKeague and Wolynetz (1980)
Canadian Interior Plains	"	(21)	Background	Plant Uptake	NR	NR	AAS	Field	McKeague and Wolynetz (1980)
Canadian Cordilleran	"	(46)	Background	Plant Uptake	NR	NR	AAS	Field	McKeague and Wolynetz (1980)
16 Manitoba Soils	Agriculture	(25) A Hor.	Background	Plant Uptake	NR	NR	AAS	Field	Mills and Zwarich (1975)
16 Manitoba Soils	Agriculture	(23) C Hor.	Background	Plant Uptake	NR	NR	AAS	Field	Mills and Zwarich (1975)
Michigan - Sand	Woodland	2.8	Background	Plant Uptake	NR	NR	AAS	Field	Klein and Russell (1973)
Residential Soils Grand Rapids, MI	Lawns and Woodlands	(8.0)	Background	NR	NR	NR	AAS	Field	Klein (1972)
Agricultural Soils, Michigan	Crops	(8.8)	Background	NR	NR	NR	AAS	Field	Klein (1972)
Industrial Soils Grand Rapids, MI	Industrial Sites	(16.3)	Background	NR	NR	NR	AAS	Field	Klein (1972)
Airport Soils		(10.4)	Background	NR	NR	NR	AAS	Field	Klein (1972)
Cottenham Sandy Loam	Onions	3.9 w/MYC[A]	Background	Plant Uptake	Onions	5 weeks	AAS	Greenhouse	Gildon and Tinker (1983)
Cottenham Sandy Loam	Onions	2.8 wo/MYC[A]	Background	Plant Uptake	Onions	5 weeks	AAS	Greenhouse	Gildon and Tinker (1983)

Table 1. Background total copper levels in soils, continued.

Medium	Use	Level (ppm DW) Means in ()	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Piedmont Weathered Bedrock	NR	13-191 (52)	Background	Plant Uptake	Forage	NR	AOAC	Field	Price et al. (1955)
Worldwide	NR	2-100 (20)	Background	NR	NR	NR	NR	Field	Bowen (1966)
Ritzville Silt Loam	Agriculture	31	Background	Plant Uptake	Crops	NR	AAS	Field	Cataldo and Wildung (1978)
Aberdeenshire, UK	NR	10-21	Background	NR	NR	NR	SSMS	Field	Ure and Bacon (1978)
Yakima Co. WA pH (7.9)	Grapes	20-30 (22)	Background	Plant Uptake	European Grapes	Maturity	ES	Field	Shacklette (1980)
San Jaquin Co. CA pH (6.4)	Grapes	15-50 (27)	Background	Plant Uptake	European Grapes	Maturity	ES	Field	Shacklette (1980)
Berrien Co. MI pH (6.6)	Orchards	10-30 (18)	Background	Plant Uptake	Apples	Maturity	ES	Field	Shacklette (1980)
Wayne Co. NY pH (5.5)	Orchards	15-30 (19)	Background	Plant Uptake	Apples	Maturity	ES	Field	Shacklette (1980)
Gloucester Co. NJ pH (5.5)	Orchards	15-30 (20)	Background	Plant Uptake	Apples	Maturity	ES	Field	Shacklette (1980)
Yakima, Co. WA pH (6.6)	Orchards	20-70 (36)	Background	Plant Uptake	Apples	Maturity	ES	Field	Shacklette (1980)
Mesa Co. CA pH (7.8)	Orchards	20-50 (31)	Background	Plant Uptake	Apples	Maturity	ES	Field	Shacklette (1980)
San Joaquin Co. CA pH (6.8)	Orchards	15-150 (100)	Background	Plant Uptake	Peaches	Maturity	ES	Field	Shacklette (1980)
Mesa Co. CO pH (7.7)	Orchards	20-30 (24)	Background	Plant Uptake	Peaches	Maturity	ES	Field	Shacklette (1980)
Mesa Co. CO pH (8.0)	Orchards	15-100 (28)	Background	Plant Uptake	Pears	Maturity	ES	Field	Shacklette (1980)
San Joaquine Co. CA pH (7.0)	Orchards	150-300 (240)	Background	Plant Uptake	Pears	Maturity	ES	Field	Shacklette (1980)
Yakima Co. WA pH (6.3)	Orchards	30-70 (44)	Background	Plant Uptake	Pears	Maturity	ES	Field	Shacklette (1980)
Wayne Co. NY pH (6.6)	Orchards	7-20 (13)	Background	Plant Uptake	Pears	Maturity	ES	Field	Shacklette (1980)
Berrien Co. MI pH (5.4)	Orchards	15-50 (25)	Background	Plant Uptake	Pears	Maturity	ES	Field	Shacklette (1980)

[A] Mycorrhiza

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Table 2. Elevated total copper levels in soils.

Medium	Use	Level (ppm DW)	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Ore Roasting Bed	Agrostis gigantea	1220-2254	1 % Ground Veg. Cover	Plant Uptake	NR	Maturity	AAS	Field	Hogan et al. (1977)
Yolo Loam	Bush Bean	500	83 % YR	$CuSO_4$	Leaf	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Yolo Loam	Bush Bean	500	69 % YR	$CuSO_4$	Stem	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Warsaw Sandy Loam	Corn	343	60 % YR[A]	$CuCl_2$/Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Warsaw Sandy Loam	Rye	343	39 % YR[A]	$CuCl_2$/Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Warsaw Sandy Loam	Corn	343	59 % YR[A]	$CuCl_2$/Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Yolo Loam	Bush Bean	200	26 % YR	$CuSO_4$	Leaf	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Yolo Loam	Bush Bean	200	14 % YR (N.S.)	$CuSO_4$	Stem	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Warsaw Sandy Loam	Corn	194	41 % YR[A]	$CuCl_2$/Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Warsaw Sandy Loam	Rye	194	29 % YR[A]	$CuCl_2$/Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Warsaw Sandy Loam	Corn	194	51 % YR[A]	$CuCl_2$/Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Warsaw Sandy Loam	Corn	150	68 % YR[B]	$CuCl_2$	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975b)
Warsaw Sandy Loam	Rye	150	43 % YR[B]	$CuCl_2$	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975b)
Warsaw Sandy Loam	Corn	150	61 % YR[B]	$CuCl_2$	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975b)
Warsaw Sandy Loam	Corn	120	45 % YR[A]	$CuCl_2$/Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Warsaw Sandy Loam	Rye	120	14 % Yield Increase[A]	$CuCl_2$/Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Warsaw Sandy Loam	Corn	120	44 % YR[A]	$CuCL_2$/Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Yolo Loam	Bush Bean	100	12 % YR (N.S.)	$CuSO_4$	Leaf	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Yolo Loam	Bush Bean	100	0.8 % YR (N.S.)	$CUSO_4$	Stem	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
"Sandy Soil"	Per Rye Grass	99	50 % YR	Cu Salts	Shoot	4 weeks	AAS	Greenhouse	Dijkshoorn et al (1979)
Cottenham Sandy Loam	Onions	75 w/MYC[C]	3.7 % YR	$CuSO_4\ 3H_2O$	Leaves	5 weeks	AAS	Greenhouse	Gildon and Tinker (1983)
Cottenham Sandy Loam	Onions	75 wo/MYC[C]	11.5 % YR	$CuSO_4\ 3H_2O$	Leaves	5 weeks	AAS	Greenhouse	Gildon and Tinker (1983)
"Sandy Soil"	Plantain	56	50 % YR	Cu Salts	Shoot	6 weeks	AAS	Greenhouse	Dijkshoorn et al (1979)
"Sandy Soil"	White Clover	52	50 % YR	Cu Salts	Shoot	8 weeks	AAS	Greenhouse	Dijkshoorn et al (1979)
Yolo Loam	Bush Bean	50	17 % YR (N.S.)	$CuSO_4$	Leaf	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Yolo Loam	Bush Bean	50	1.1 % YR (N.S.)	$CuSO_4$	Stem	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Warsaw Sandy Loam	Corn	46	68 % Yield Increase (crop 1)	Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975b)
Warsaw Sandy Loam	Rye	46	96 % Yield Increase (crop 2)	Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975b)
Warsaw Sandy Loam	Corn	46	17 % YR (crop 3)	Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975b)
Cottenham Sandy Loam	Onions	30 w/MYC[C]	2.8 % YR	$CuSO_4\ 3H_2O$	Leaves	5 weeks	AAS	Greenhouse	Gildon and Tinker (1983)
Cottenham Sandy Loam	Onions	30 wo/MYC[C]	16 % YR	$CuSO_4\ 3H_2O$	Leaves	5 weeks	AAS	Greenhouse	Gildon and Tinker (1983)
Cottenham Sandy Loam	Onions	15 w/MYC[C]	5.5 % YR	$CuSO_4\ 3H_2O$	Leaves	5 weeks	AAS	Greenhouse	Gildon and Tinker (1983)
Cottenham Sandy Loam	Onions	15 wo/MYC[C]	5.7 % YR	$CuSO_4\ 3H_2O$	Leaves	5 weeks	AAS	Greenhouse	Gildon and Tinker (1983)
Cottenham Sandy Loam	Onions	5 w/MYC[C]	7 % Yield Increase	$CuSO_4\ 3H_2O$	Leaves	5 weeks	AAS	Greenhouse	Gildon and Tinker (1983)
Cottenham Sandy Loam	Onions	5 wo/MYC[C]	3.8 % YR	$CuSO_4\ 3H_2O$	Leaves	5 weeks	AAS	Greenhouse	Gildon and Tinker (1983)

[A] Other metal levels: Zn - 410 ppm, Cr - 404 ppm, Ni - 37 ppm
[B] Other metal levels: Zn - 300 ppm, Cr - 350 ppm, Ni - 15 ppm
[C] Mycorrhiza

2.1.2 Copper levels in plants

Copper is known to be an essential nutrient for both plants and animals and, except for molybdenum, is the least abundant essential nutrient in soil. Most problems involve copper deficiency in plants or animals and copper toxicosis is uncommon except in mineralized areas or zones polluted by mining and smelting activities (Gough et al. 1979, Hutchinson 1979).

Uptake of copper increases with increased copper levels in soil (Wallace et al. 1977a). Absorption of copper is thought to be active but passive absorption may also occur, especially under conditions of high soil copper concentrations (Kabata-Pendias and Pendias 1984).

Copper concentrations have been found to be markedly higher in plant roots as opposed to above ground parts (Agarwala et al. 1977, Chino 1981, Forbes 1917 and Jarvis 1978). Plant roots exhibit a strong capability to hold copper under both deficiency and toxic conditions (Kabata - Pendias and Pendias 1984). Jarvis (1978) reported that up to 96 percent of the total plant copper content of ryegrass is retained by roots under high uptake conditions and the copper held by roots is not available to ryegrass shoots even after a further supply of copper is withdrawn. Toxic concentrations in root are only negligibly translocated to the above ground biomass (Bennett 1971) probably because copper in plant roots is insoluble in its association with cell walls (Jarvis 1978).

Copper toxicity in plants is produced from several factors: 1) root tissue damage, which restricts root extension, membrane permeability and inhibits translocation of iron (Bennett 1971, Kabata - Pendias and Pendias 1984); 2) Peroxidation of chloroplast membrane lipids and inhibition of photosynthetic electron transport (Kabata - Pendias and Pendias 1984); and 3) immobilization of copper in cell walls, cell vacuoles and nondiffusible copper-protein complexes (Kabata - Pendias and Pendias 1984). Elevated copper concentrations also adversely affect potassium uptake in cereal grains (Bujtas and Cseh 1981).

The first symptom of copper toxicity is depressed growth (Dijkshoorn et al. 1979) and retarded germination, seedling growth, and root development (Forbes 1917, Chapman et al. 1940, Reuther et al. 1952, Reitz and Shimp 1953, Dekock 1956). Copper toxicity results in an induced iron chlorosis, depressed tillering and thick, short, barbed-wire roots (Agarwala et al. 1977, Bennett 1971, Chino 1981, Reilly and Reilly 1973). Sensitive crops are cereals, legumes, spinach and citrus seedlings.

Copper has been shown to be synergistic with zinc, nickel and cadmium in solustion culture experiments using bush beans (Wallace and Romney 1977c). "Copper, nickel and cadmium were more toxic together than any one alone". These authors also noted a synergistic effect (decreased levels of phosphorus, zinc and iron in bush bean roots) when copper and nickel were applied together in solution culture experiments.

A major factor influencing copper toxicity in plants is the variation exhibited by different plant species in uptake and susceptibility to copper toxicosis. Leguminous plants seem particularly sensitive to high concentrations of copper. This is due to the inhibitory effect of copper on root nodulation and fixation (Vesper and Weidensaul 1978, Porter and Sheridan 1981). Vesper and Weidensaul (1978) reported that copper at all levels tested had adversely impacted dry weights of stems and foliage. Copper treatments of 5 and 10 ppm decreased nitrogen fixation 39 and 46 percent respectively. All copper levels reduce nodulation. Porter and Sherdian (1981) reported nitrogen fixation was eliminated in alfalfa at solution concentrations of 100 ug copper/ml.

In contrast there are some plants which are tolerant to elevated copper levels. Wallace et al. (1977e) found that 51.2 ppm copper (in shoots) had no adverse impact upon the vegetative yield of rice plants. Hogan and Rauser (1979) found that a 50 percent reduction in yield occurred in non-tolerant clones of *Agrostics gigantea* at concentrations of 8 mmol/m^{-3}, while this level of reduced growth was not reached by the tolerant clone until concentrations exceeded 40 mmol/m^{-3}. Haque and Subramanian

(1982) reported that the yield of perennial ryegrass was reduced after the dry matter accumulation of copper exceeded 40 ppm.

Typical background concentrations of grasses and legumes are 5 and 15 ppm respectively (Table 3). Price et al. (1955) measured a copper concentration range of 1.5 ppm (timothy) to 29.0 ppm (red clover) in the Piedmont area of Virginia. Elevated levels of copper in vegetation range up to 1457 ppm found in the roots of copper tolerant clones of Agrostis gigantea (Hogan and Rause, 1979). These authors reported shoot copper concentrations of 487 to 801 ppm in the tolerant clones of this species. Levels considerably below these concentrations are phytotoxic to many plants (Table 4). Selection of phytotoxic criteria for copper in plants is discussed in section 3.1.

2.2 Mercury Levels in Soils and Plants

Mercury, the only liquid metal at normal temperatures of the earth's surface, is present in trace amounts in most geological materials, soils and plants (Connor and Shacklette 1975, Lagerwerff 1972, Shacklette and Boerngen 1984, Smart 1968, Vostal 1972, Wedepohl 1978). This element is very toxic to fungi and most plants as well as higher animals including man (Bowen 1966, Cook 1977, D'Itri 1972). Mercury ore deposites are found in geologically active belts, including the Pacific rim and a belt through Asia and the Mediterranean. The largest and richest deposits have been found in Spain (D'Itri 1972). Mercury is also known to be associated with many hydrothermal ore deposits of precious and base metals and has been used for geochemical prospecting for such deposits (Fleischer 1970, Oftedal 1940, McCarthy et al. 1969, Warren et al. 1966).

Annual global mobilization of mercury into the atmosphere has been estimated at 25,000 and 11,000 to 20,000 metric tons for natural and anthropogenic sources respectively (Galloway et al. 1982). Major sources of anthropogenic mercury include mining and smelting, manufacturing, combustion of fossil fuels, chlor-alkali plants, sewage disposal and agriculture (Blackwood et al. 1979, Bull et al. 1977, Cappon 1984, Crockett and Kinnison 1979, D'Itri

Table 3. Background copper levels in plants.

Medium	Use	Level (ppm DW)	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
U.S. Soils	Red Clover	(10.0)[A]	Background	Plant Uptake	Above Ground Biomass	NR	HNO_3/Dithizone	Field	Kubota (1983)
U.S. Soils	Alfalfa	(8.8)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
U.S. Soils	Alsike Clover	(8.3)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
U.S. Soils	Sweet Clover	(7.9)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
U.S. Soils	Ladino Clover	(7.9)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
U.S. Soils	Lotus	(7.4)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
U.S. Soils	Smooth Brome	(5.9)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
U.S. Soils	Bluegrass	(5.5)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
U.S. Soils	Orchard Grass	(5.2)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
U.S. Soils	Timothy	(4.6)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
U.S. Soils	Fescue	(4.4)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
U.S. Soils	Wheatgrass	(4.0)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
U.S. Soils	Broomsedge	(1.5)	Background	Plant Uptake	"	NR	AAS	Field	Kubota (1983)
Lateritic Gravelly Sand, pH 5.0	Trifolium hirtum	5.3-12.3	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Ornithopus sativus	7.2-8.9	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Pisum arvense	7.4-8.4	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Lupinus consentinii	5.8-8.8	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Ornithopus compressus	7.0-8.1	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Sub. clover	6.2-10.7	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Alfalfa	5.1-7.6	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Lupinus luteus	4.6-8.5	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Vicia atropurpurea	5.6-8.0	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Lupinus albus	3.2-6.8	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Lupinus angustifolia	3.0-6.0	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Arctotheca calendula	6.2-16.5	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Rye	4.5-8.5	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Wheat	3.3-5.6	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Barley	2.5-5.4	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Oats cv Ballidu	2.4-6.8	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Oats cv Avon	2.4-7.6	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Bromus rigidus	3.9-9.7	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Lateritic Gravelly Sand, pH 5.0	Bromus mollis	3.8-6.6	Background	Plant Uptake	"	3-5 months	AAS	Field	Gladstones et al. (1975)
Piedmont Soils	Alfalfa	6.5-19.7	Background	Plant Uptake	"	Maturity	AOAC	Field	Price et al. (1955)
Piedmont Soils	Lespedeza	6.0-14.2	Background	Plant Uptake	"	(July-Aug)	AOAC	Field	Price et al. (1955)
Piedmont Soils	Red Clover	10.5-29.0	Background	Plant Uptake	"	"	AOAC	Field	Price et al. (1955)
Piedmont Soils	Ladino Clover	10.2-15.2	Background	Plant Uptake	"	"	AOAC	Field	Price et al. (1955)
Piedmont Soils	Timothy	1.5-9.7	Background	Plant Uptake	"	"	AOAC	Field	Price et al. (1955)
Piedmont Soils	Orchard Grass	8.0-18.5	Background	Plant Uptake	"	"	AOAC	Field	Price et al. (1955)
Cottenham Sandy Loam	Onions	3.9 w/MYC[B]	Background	Plant Uptake	Leaves	5 weeks	AAS	Field	Gildon and Tinker (1983)
Cottenham Sandy Loam	Onions	2.8 wo/MYC[B]	Background	Plant Uptake	Leaves	5 weeks	AAS	Field	Gildon and Tinker (1983)

[A] ( ) denotes means

[B] Mycorrhiza

Table 3. Background copper levels in plants, continued.

Medium	Use	Level (ppm DW)	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
U.S. Soils	Cabbage (Wi)	20-150 (29) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Corn (Ga)	70-150 (100) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Corn (Mo)	50-100 (70) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Cucumber (Wi)	60-120 (77) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Potato (Wi)	40-150 (94) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Soybean (Mo)	100-200 (170) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Tomato (Ga)	30-150 (79) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Black Cherry (Ga)	70-500 (170) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Buckbush (Mo)	100-1500 (190) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Cedar (Mo)	20-200 (50) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Shagbark Hickory (Ky)	50-500 (130) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Black Oak (Ky)	70-500 (120) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	White Oak (Ky)	70-200 (130) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Smooth Sumac (Mo)	50-200 (110) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
U.S. Soils	Winged Sumac	50-200 (110) AWT	Background	Plant Uptake	Plant Uptake	NR	AAS	Field	Conner et al. (1976)
Sand Culture	Barley	12.4	Background	Plant Uptake	Roots	9 weeks	CCM	Greenhouse/Nut. Soil	Agarwala et al. (1977)
Sand Culture	Barley	4.6	Background	Plant Uptake	Young Leaves	9 weeks	CCM	Greenhouse/Nut. Soil	Agarwala et al. (1977)
Sand Culture	Barley	3.8	Background	Plant Uptake	Old Leaves	9 weeks	CCM	Greenhouse/Nut. Soil	Agarwala et al. (1977)
Sand Culture	Barley	2.8	Background	Plant Uptake	Stem	9 weeks	CCM	Greenhouse/Nut. Soil	Agarwala et al. (1977)
Solution Culture	Bush Beans	7.4	Background	Plant Uptake	Leaves	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977d)
Solution Culture	Bush Beans	3.7	Background	Plant Uptake	Stems	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977d)
British Columbia Soils	Timber Milk Vetch	2.8-9.0 (6.1)	Background	Plant Uptake	Above Ground Biomass	NR	AAS	Field	Fletcher and Brink (1969)
"	Arnica	4.5-8.5 (6.4)	Background	Plant Uptake	"	NR	AAS	Field	Fletcher and Brink (1969)
"	Pinegrass	4.5-10.2 (7.2)	Background	Plant Uptake	"	NR	AAS	Field	Fletcher and Brink (1969)
"	Kentucky Bluegrass	7.9-14.1 (9.9)	Background	Plant Uptake	"	NR	AAS	Field	Fletcher and Brink (1969)
"	Wheatgrass	3.7-7.9 (6.2)	Background	Plant Uptake	"	NR	AAS	Field	Fletcher and Brink (1969)
"	Lupine	7.9-8.5 (8.2)	Background	Plant Uptake	"	NR	AAS	Field	Fletcher and Brink (1969)
Polluted Soils	Agrostis gigantea	48-89	Background near Sudbury	Plant Uptake	Shoots	Maturity	AAS	Field	Hogan et al. (1977)
Soil	Tall Fescue	3.3-10.2	Background (Penn)	Plant Uptake	Above Ground Biomass	NR	NR	Field	Sopper and Seaker (1984)
Organic Muck Soils	Lettuce	(3.6) - (5.4)	Background(Ont)	Plant Uptake	Leaves	NR	AAS	Field	Czuba and Hutchinson (1980)
"	Lettuce	(18.4) - (29.0)	"	Plant Uptake	Roots	NR	AAS	Field	Czuba and Hutchinson (1980)
"	Celery	(4.6) - (6.4)	"	Plant Uptake	Leaves	NR	AAS	Field	Czuba and Hutchinson (1980)
"	Celery	(13.8) - (25.5)	"	Plant Uptake	Roots	NR	AAS	Field	Czuba and Hutchinson (1980)
"	Carrots	(4.8) - (6.5)	"	Plant Uptake	Leaves	NR	AAS	Field	Czuba and Hutchinson (1980)
"	Carrots	(6.5) - (17.0)	"	Plant Uptake	Roots	NR	AAS	Field	Czuba and Hutchinson (1980)
"	Lettuce	(8.7)	"	Plant Uptake	Leaf	Maturity/ Autumn	AAS	Field	Czuba and Hutchinson (1980)
"	Lettuce	(24.0)	"	Plant Uptake	Root	"	AAS	Field	Czuba and Hutchinson (1980)
"	Celery	(7.8)	"	Plant Uptake	Leaf/Stalk	"	AAS	Field	Czuba and Hutchinson (1980)
"	Celery	(12.6)	"	Plant Uptake	Root	"	AAS	Field	Czuba and Hutchinson (1980)
"	Potato	(11.1)	"	Plant Uptake	Leaf	"	AAS	Field	Czuba and Hutchinson (1980)
"	Potato	(10.9)	"	Plant Uptake	Roots/Tubers	"	AAS	Field	Czuba and Hutchinson (1980)
"	Carrot	(6.9)	"	Plant Uptake	Leaf	"	AAS	Field	Czuba and Hutchinson (1980)
"	Carrot	(4.9)	"	Plant Uptake	Root	"	AAS	Field	Czuba and Hutchinson (1980)
"	Parsnip	(8.9)	"	Plant Uptake	Leaf	Spring	AAS	Field	Czuba and Hutchinson (1980)
"	Parsnip	(8.9)	"	Plant Uptake	Root	Spring	AAS	Field	Czuba and Hutchinson (1980)
"	Onion	(4.3)	"	Plant Uptake	Leaf	Maturity/ Autumn	AAS	Field	Czuba and Hutchinson (1980)
"	Onion	(24.1)	"	Plant Uptake	Root	"	AAS	Field	Czuba and Hutchinson (1980)
"	Onion	(3.7)	"	Plant Uptake	Bulb	"	AAS	Field	Czuba and Hutchinson (1980)
"	Cauliflower	(3.9)	"	Plant Uptake	Leaf	"	AAS	Field	Czuba and Hutchinson (1980)
"	Cauliflower	(8.6)	"	Plant Uptake	Root	"	AAS	Field	Czuba and Hutchinson (1980)
"	Cauliflower	(4.5)	"	Plant Uptake	Flower Head	"	AAS	Field	Czuba and Hutchinson (1980)
"	Cabbage	(2.9)	"	Plant Uptake	Leaf	"	AAS	Field	Czuba and Hutchinson (1980)
"	Cabbage	(7.7)	"	Plant Uptake	Root	"	AAS	Field	Czuba and Hutchinson (1980)

Table 3. Background copper levels in plants, continued.

Medium	Use	Level (ppm DW)	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Plainfield Loamy Sand	Snap Beans	16.7-18.3	Background	Plant Uptake	Leaves	First Trifoliate Leaf	AAS	Field	Walsh et al. (1972)
"	Snap Beans	8.3-24.7	"	Plant Uptake	Leaves	Pod Set	AAS	Field	Walsh et al. (1972)
"	Snap Beans	14.3-17.0	"	Plant Uptake	Leaves	Maturity	AAS	Field	Walsh et al. (1972)
"	Snap Beans	10.7-16.0	"	Plant Uptake	Stems	Maturity	AAS	Field	Walsh et al. (1972)
"	Snap Beans	12.0-18.0	"	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Solution Culture	Per. Ryegrass	3.8	Background	Plant Uptake	Shoots	21 Days	AAS	Greenhouse	Jarvis (1978)
Frilsham Loam	Per. Ryegrass	8.8	Background	Plant Uptake	Shoots	42-102 days	AAS	Greenhouse	Jarvis (1978)
Frilsham Loam	Per. Ryegrass	12.6	Background	Plant Uptake	Roots	102 days	AAS	Greenhouse	Jarvis (1978)
Ritzville Silt Loam	Soybeans	3.90	Background	Plant Uptake	Tops	60 days	AAS	Greenhouse	Cataldo and Wildung (1978)
Hubbard Coarse Sand	Snap Beans	4.1	Background (Unfert)	Plant Uptake	Pods	Maturity	AAS	Field	Latterell et al. (1978)
"	Snap Beans	2.8	Background (Fert)	Plant Uptake	Pods	Maturity	AAS	Field	Latterell et al. (1978)
"	Snap Beans	10.0	Background (Unfert)	Plant Uptake	Leaves	Early Bloom Stage	AAS	Field	Latterell et al. (1978)
"	Snap Beans	8.2	Background (Fert)	Plant Uptake	Leaves	"	AAS	Field	Latterell et al. (1978)
U.S. Soils	Lettuce	1.6-18.3 (6.3)	Background	Plant Uptake	Edible Portions	NR	ICP	Field	Wolnik et al. (1983)
U.S. Soils	Peanuts	0.91-22 (8.6)	Background	Plant Uptake	"	NR	ICP	Field	Wolnik et al. (1983)
U.S. Soils	Potatoes	0.73-14 (5.0)	Background	Plant Uptake	"	NR	ICP	Field	Wolnik et al. (1983)
U.S. Soils	Soybeans	3.5-29 (12)	Background	Plant Uptake	"	NR	ICP	Field	Wolnik et al. (1983)
U.S. Soils	Wheat	2.5-9.9 (5.0)	Background	Plant Uptake	"	NR	ICP	Field	Wolnik et al. (1983)
U.S. Soils	Sweet Corn	0.89-4.3 (2.1)	Background	Plant Uptake	"	NR	ICP	Field	Wolnik et al. (1983)

Table 4. Elevated copper levels in plants.

Medium	Use	Level (ppm DW)	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Sand Culture	Barley	2120	31 % YR	$CuSO_4$ $5H_2O$	Roots	6 weeks	CC	Greenhouse	Agarwala et al. (1977)
Frilsham Loam	Perennial Ryegrass	377.3	49 % YR	Plant Uptake $Cu(NO_3)_2$ $3H_2O$	Roots	102 days	AAS	Greenhouse	Jarvis (1978)
Sand Culture	Barley	156	34 % YR	$CuSO_4$ $5H_2O$	Old Leaves	6 weeks	CC	Greenhouse	Agarwala et al. (1977)
Warsaw Sandy Loam	Corn	127.8	60 % YR	Amended Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Frilsham Loam	Perennial Ryegrass	94.7	7.8 % YR	Plant Uptake	Roots	102 days	AAS	Greenhouse	Jarvis (1978)
Sand Culture	Oats	92	Specific Cu Tox. 44 % Reduction in Plant Height	$CuSO_4$ $5H_2O$	Shoots	40 days	Spectro-chemical	Greenhouse	Hunter and Vergnano (1953)
Warsaw Sandy Loam	Corn	83.8	41 % YR	Amended Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Warsaw Sandy Loam	Corn	56.1	45 % YR	Amended Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Warsaw Sandy Loam	Rye	53.8	39 % YR	Amended Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Sand Culture	Barley	52	34 % YR	$CuSO_4$ $5H_2O$	Stem	6 weeks	CC	Greenhouse	Agarwala et al. (1976)
NR	Cabbage	50	Reduced Yield	NR	NR	NR	NR	NR	Hara and Sonoda (1979)
Sand Culture	Barley	49	34 % YR	$CuSO_4$ $5H_2O$	Young Leaves	6 weeks	CC	Greenhouse	Agarwala et al. (1976)
Warsaw Sandy Loam	Corn	43.7	59 % YR	Amended Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
"Sandy Soil"	White Clover	37	50 % YR	Plant Uptake	Shoots	8 weeks	AAS	Greenhouse	Dijkshoorn et al (1979)
Sand Culture	Oats	37	Highly Chloratic 13 % Reduction in Plant Height	$CuSO_4$ $5H_2O$	Shoots	40 days	Spectro-chemical	Greenhouse	Hunter and Vergnano (1953)
Warsaw Sandy Loam	Corn	35.1	51 % YR	Amended Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Yolo Loam	Bush Bean	34.3	83 % YR	Plant Uptake	Leaves	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Warsaw Sandy Loam	Rye	30.9	29 % YR	Amended Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Warsaw Sandy Loam	Corn	30.5	44 % YR	Amended Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Yolo Loam	Bush Bean	28.8	26 % YR	Plant Uptake	Leaves	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Plainfield Loamy Sand	Snap Beans	27.3	84 % YR	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Warsaw Sandy Loam	Rye	26.1	14 % Yield Increase	Amended Sludge	Above Ground Biomass	6 weeks	AAS	Greenhouse	Cunningham et al. (1975a)
Frilsham Loam	Perennial Ryegrass	25.5	6.9 % YR	Plant Uptake	Shoots	102 days	AAS	Greenhouse	Jarvis (1978)
Solution Culture	Perennial Ryegrass	24.7	3.4 % YR	$CuSO_4$ $5H_2O$	Shoots	21 days	AAS	Greenhouse	Jarvis (1978)
Plainfield Loamy Sand	Snap Beans	20.7	38 % YR	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Yolo Loam	Bush Bean	20.3	69 % YR	Plant Uptake	Stem	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Plainfield Loamy Sand	Snap Beans	20.0	17 % YR (N.S.)	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Plainfield Loamy Sand	Snap Beans	19.6	34 % YR	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Plainfield Loamy Sand	Snap Beans	18.7	5 % YR (N.S.)	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Sand Culture	Barley	18-21 (20)	10 % YR	Plant Uptake	Shoot	5 leaf stage	AAS	Greenhouse	Davis and Beckett (1978)
"Sandy Soil"	Perennial Ryegrass	18	50 % YR	Plant Uptake	Shoot	4 weeks	AAS	Greenhouse	Dijkshoorn et al (1979)
Yolo Loam	Bush Bean	17.8	12 % YR (N.S.)	Plant Uptake	Leaves	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Plainfield Loamy Sand	Snap Beans	17.7	24 % YR (N.S.)	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Plainfield Loamy Sand	Snap Beans	17.3	6.5% Yield Increase (N.S.)	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Plainfield Loamy Sand	Snap Beans	17	4 % YR (N.S.)	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Sand Culture	Oats	17	Normal	$CuSO_4$ $5H_2O$	Shoots	40 days	Spectro-chemical	Greenhouse	Hunter and Vergnano (1953)
Plainfield Loamy Sand	Snap Beans	16.3	14 % YR (N.S.)	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Frilsham Loam	Perennial Ryegrass	15.3	7.8 % YR	Plant Uptake $Cu(NO_3)_2$ $3H_2O$	Shoots	42-102 days	AAS	Greenhouse	Jarvis (1978)
Plainfield Loamy Sand	Snap Beans	15	76 % YR	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Plainfield Loamy Sand	Snap Beans	15	1.6 % YR (N.S.)	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
"Sandy Soil"	Plantain	15	50 % YR	Plant Uptake	Shoots	6 weeks	AAS	Greenhouse	Dijkshoorn et al (1979)

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Table 4. Elevated copper levels in plants, continued.

Medium	Use	Level (ppm DW)	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Frilsham Loam	Perennial Ryegrass	14.7	49 % YR	Plant Uptake $Cu(NO_3)_2\ 3H_2O$	Shoots	42-102 days	AAS	Greenhouse	Jarvis (1978)
Solution Culture	Perennial Ryegrass	14.2	17.6% Yield Increase	$CuSO_4\ 5H_2O$	Shoots	21 days	AAS	Greenhouse	Jarvis (1978)
Plainfield Loamy Sand	Snap Beans	13.7	21 % YR (N.S.)	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Plainfield Loamy Sand	Snap Beans	12.3	1.5 % Yield Increase (N.S.)	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Plainfield Loamy Sand	Snap Beans	12.3	3 % YR (N.S.)	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Yolo Loam	Bush Bean	11.7	14 % YR (N.S.)	Plant Uptake	Stem	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Plainfield Loamy Sand	Snap Beans	11	26 % Yield Increase	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Solution Culture	Perennial Ryegrass	10.7	13 % Yield Increase	$CuSO_4\ 5H_2O$	Shoots	21 days	AAS	Greenhouse	Jarvis (1978)
Plainfield Loamy Sand	Snap Beans	10.3	15 % Yield Increase (N.S.)	Plant Uptake	Pods	Maturity	AAS	Field	Walsh et al. (1972)
Yolo Loam	Bush Bean	10	17 % YR (N.S.)	Plant Uptake	Leaves	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Yolo Loam	Bush Bean	9.5	0.8 % YR (N.S.)	Plant Uptake	Stem	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Solution Culture	Perennial Ryegrass	5.9	7.3 % Yield Increase	$CuSO_4\ 5H_2O$	Shoots	21 days	AAS	Greenhouse	Jarvis (1978)
Yolo Loam	Bush Bean	5.0	1.1 % YR (N.S.)	Plant Uptake	Stem	17 days	ES	Greenhouse/Soil Pots	Wallace et al. (1977a)
Sand Culture	Soybeans	3.22	27 % YR	Cu Solution	Shoots	42 days	AAS	Greenhouse	Vesper and Weidensaul (1978)
Sand Culture	Soybeans	3.15	11 % YR	Cu Solution	Shoots	42 days	AAS	Greenhouse	Vesper and Weidensaul (1978)

1972, Lindberg and Turner 1977, Lindberg et al. 1979). Typical condenser stack gas emissions from primary lead smelters of 0.12 Kg mercury per metric ton of lead ore, have been reported (Blackwood et al. 1979). Agricultural use of mercury for seed treatments and fungicides has decreased in recent years due to environmental concerns and the danger of mercury entering the food chain (Friberg and Vostal 1972).

Mercury is found in three valence states: metallic Hg, Hg^+ and Hg^{++} and forms hundreds of inorganic and organic compounds (Battelle 1977). Mercury has received very little attention concerning the existence and levels of specific chemical forms which could influence the soil chemistry and eventual plant uptake (Cappon 1984). The three common forms of mercury; elemental, inorganic salts, and organic compounds, are all toxic but the organic compounds, especially the alkyl mercury compounds, appear the most hazardous (Blackwood et al. 1979). The toxicity of mercury to terrestrial plants apparently depends more on chemical form than on its concentration (Ratsch 1974).

2.2.1 Total mercury levels in soils

Mercury is immobilized in soils through three basic processes: 1) formation of relatively insoluble forms such as HgS, metallic Hg and Hg_2^{2+}; 2) sorption by soil colloids, especially clays; and 3) complexation by organic ligands (Gilmour and Miller 1973, Hogg et al. 1978, Kabata-Pendias and Pendias 1984, Lindberg et al. 1979, Weaver et al. 1984). Accumulation of mercury in soils is controlled by organic complex formation and by precipitation (Kabata-Pendias and Pendias 1984). Mercury is usually retained in soils as slightly mobile organocomplexes (Kabata-Pendias and Pendias 1984) and organic soils generally have elevated mercury levels compared to mineral soils (Chattopadhyay and Jervis 1974, Frank et al. 1976). Lindberg et al. (1979) reported a control soil (pH 5.6) in the vicinity of the Almaden mercury deposit in Spain in which organo-clay complexes contained 38 percent of the soil mercury distribution, and the clay-mineral fraction and mineral fraction contained 35 percent and 6 percent of the soil mercury respectively. Dudas and Pawluk (1977) found a significant relationship between mercury levels and 1) cation exchange capacity (CEC), 2) organic matter content and 3) exchangeable calcium only in poorly drained soils. These authors found no significant relationships between soil mercury levels and pH, organic matter content, CEC or exchangeable calcium for well drained or solonetz soils. This may have been partially due to the low mercury levels found in this study (only one sample >0.060 ppm mercury).

Mercury levels in soils may be decreased by three general mechanisms: 1) volatilization, 2) leaching, and 3) plant uptake. Mercury in soils is unique in that it is one of the few metals that is readily volatilized and lost to the atmosphere from surface soils (Frear and Dills 1967, Gilmour and Miller 1973, Lindberg et al. 1979). Estimates of mercury volatilization range from 10 to 32 percent and 44 to 56 percent by Hogg et al. (1978) and Gilmour and Miller (1973) respectively. Lindberg et al. (1979) measured 0.13 and 0.33 ug mercury/m^2 volatilization per hour at 25°C from background soils and soils near the Almadin mercury mine respectively. Hogg et al. (1978) determined 10 to 32 percent of all applied soil mercury in their experiments was lost presumably by volatilization. The formation of volatile mercury has been shown to be stimulated by increased soil moisture, pH, and temperature (Frear and Dills 1967, Gilmour and Miller 1973).

Leaching of mercury from surface soils is limited but apparently does occur. Significant movement of spiked mercuric chloride has been demonstrated from the 0 to 10 cm soil layer to the 20 to 30 cm soil layer and 30 to 40 cm soil layer for loam and loamy sand soils respectively (Hogg et al. 1978). However, these authors found the movement of mercuric chloride, phenyl-mercuric acetate (PMA), and methyl mercuric chloride (MMC) to be "severely limited" even in light textured soils of low organic content. No statistical significance between mercury levels in A and C horizons of 16 Manitoba soil series (loamy through clay soils) was found by Mills and Zwarich (1975). Mercury levels in rangeland soils of the Powder River Basin are only slightly higher in subsoils than in surface soils (Connor et al. 1976). Most mercury deposited on soil is confined to the upper 3 cm (Battelle 1977) and is usually present in surface soils at several times the levels in subsoils (Kabata-Pendias and Pendias 1984).

Mercury removal from the soil system by plant uptake is also limited. Very high mercury concentrations have been found in roots of several species of plants. Roots of rice plants were reported to contain 1000 ppm mercury while the grain from these plants contained only 0.5 ppm mercury (Ishizuka and Tanaka 1962). Roots of most grain crops and many vegetable crops remain in the soil and hence, much of the mercury uptake by plants remains in the soil system. Only the amount translocated to the above ground biomass is readily removed (Section 2.3.2).

The predominate form of inorganic mercury is likely to be $Hg(OH)_2$ at pH $\geq$ 7 (Kabata-Pendias and Pendias 1984). Acid gley soils may contain HgS (cinnibar) or metallic mercury (Kabata-Pendias and Pendias 1984). Methylation of inorganic mercury has been confirmed in agricultural soils (Cappon 1984). Methylmercury formation in soils is apparently directly proportional to clay and soil organic content, moisture content, temperature and substrate mercury concentrations (Cappon 1984). The process is enhanced by pH levels <6.0.

The effect of soil mercury on mycorrhizal activity is uncertain but it has been shown that additions of zinc, copper, nickel or cadmium can adversely affect mycorrhizal fungus and thus the phosphorus nutrition of the host (Gildon and Tinker 1983). Given the known toxicity of mercury and its use as a fungicide, it is quite likely that a similar response would occur from elevated soil mercury levels. This subject needs further research.

Mercury levels in the earth crust or lithosphere have been estimated from 0.05 to 0.5 ppm (Jenkins 1980, Swaine 1955). Typical values reported for sandstones, shales and carbonates are 0.030 ppm, 0.400 ppm and 0.040 ppm respectively (Wedepohl 1978)

(Table 5). Typical soil mercury levels are reported to range from 0.03 to 0.8 (Bowen 1966, Swaine 1955). Ratsch (1974) reported a United States soil mercury range of 0.10 to 0.500 ppm and most background soil mercury levels found in the literature fall within this range (Table 5). Frank et al. (1976), Mills and Zwarich (1975) and Dudas and Pawluk (1977) determined background mercury levels in soils of Ontario, Manitoba and Alberta respectively. The maximum range for these provinces was 0.01 to 0.78 ppm mercury with a maximum mean value of 0.41 ppm mercury found in an Ontario organic soil. Mean values for all Ontario and Manitoba soils tested were 0.07 and 0.033 ppm respectively. The only background mercury soil level exceeding 0.78 ppm was associated with organic muck (gley) soils in which the mercury content ranged from 1.97 ppm at the soil surface to 1.20 ppm at the 22.5 to 30 cm depth increment (Chattopadhyay and Jervis 1974). Background mercury levels for surface soils in the Powder River Basin of Montana and Wyoming were reported to range from 0.01 to 0.04 ppm with a geometric mean of 0.020 (Connor et al. 1976). Background surface soil sample sites near the Helena Valley had a reported mercury range of 0.06 to 0.12 ppm with a mean value of 0.08 (EPA 1986).

Elevated soil mercury levels have been documented near industrial sites and urban areas (Table 6). Carey et al. (1980) found significant differences between urban and suburban soils for 5 midwestern and eastern cities in the United States. The absolute values derived in this study were questionable due to the soil drying methods employed. Klein (1972) found mercury levels in soils of the Grand Rapids Michigan area of 0.10 and 0.11 ppm for residential and agricultural soils respectively. This author also reported to 0.14 and 0.33 ppm mean soil mercury concentrations for industrial sites and an airport respectively. Klein and Russell (1973) found increased soil mercury levels (0.0079 versus 0.00102 ppm) near a coal fired power plant in Michigan.

Elevated soil mercury levels have been found near many smelters and ore deposites (Heilman and Ekuan 1977, Lindberg et

Table 5. Background total mercury levels in soils.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Biotite	Not Given	0.01-0.38	Background	NR	NR	Not Applicable	NR	Field samples	Wedepohl et al. (1978)
Garnet	"	0.006-0.007	"	NR	NR	"	NR	"	"
Staurolite	"	0.005-0.963	"	NR	NR	"	NR	"	"
Sillimanite	"	0.002-2.535	"	NR	NR	"	NR	"	"
Shales	"	0.400	"	NR	NR	"	NR	"	"
Sandstones	"	0.030	"	NR	NR	"	NR	"	"
Carbonates	"	0.040	"	NR	NR	"	NR	"	"
Coal (Bit)	Fuel	0.008-0.022	"	NR	NR	"	NR	"	"
Coal (Brown)	Fuel	0.001-0.025	"	NR	NR	"	NR	"	"
Lithosphere	Not Given	0.5	"	NR	NR	"	NR	NR	Swaine (1969)
Soils	"	0.03	"	NR	NR	"	NR	NR	"
"	"	0.01-0.3	"	NR	NR	"	NR	NR	Bowen (1966)
"	"	(0.071)	"	NR	NR	"	NR	Field	Shacklette and Boerngen (1984
Soils, U.S.	"	0.010-0.500	"	NR	NR	"	FLAAS	"	Ratsch (1974)
Earth Crust	"	0.05	"	NR	NR	"		"	Jenkins (1980)
Soil, pH 7.4	Garden	0.156	"	Plant uptake	Humans	"	GLC	"	Cappon (1984)
Uncultivated Soil	Not Given	0.045-0.160	"	"	NR	"		"	Erdman et al. (1976)
Unmineralized CA soils	"	0.02-0.06	"	NR	NR	"		"	Fleischer (1970)
Soil	"	0.01	"	NR	NR	"	NR	"	EPA (1984)
" (Japan)	"	0.28	"	Plant uptake	NR	"	NR	"	Kitagishi and Yamane (1981)

Table 5. Background total mercury levels in soils, continued.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Muck soil (Sur)	Market Garden	1.97	Background	Plant uptake	Humans	Not Applicable	IPAA	Field	Chattopadhyay and Jervis (1974)
" 0-7.5 cm	"	1.18	"	"	"	"	"	"	"
" 7.5-15 cm	"	1.62	"	"	"	"	"	"	"
" 15-22.5 cm	"	1.80	"	"	"	"	"	"	"
" 22.5-30 cm	"	1.20	"	"	"	"	"	"	"
Soil, 0-4 inch	Crops/Range	(0.08)	"	"	Crops/ forage	"	EPA CV	"	EPA (1986)
Helena Valley pH 8.0	"	0.06-0.12	"	"	"	"	"	"	"
Sur Soil/Powder	Native Range	(0.020) Geometric	"	"	Sagebrush	"	AAS	"	Connor et al. (1976)
River Basin	"	0.01-0.04	"	"	"	"	"	"	"
Subsoil/Powder	"	(0.023) Geometric	"	"	"	"	"	"	"
River Basin	"	0.01-0.04	"	"	"	"	"	"	"
Soils UK	Agriculture	0.04-0.19 (0.106)	"	"	Grass	"	"	"	Bull et al. (1977)
New York Soils	Orchards	0.2	"	"	Garden Plants	Maturity	FLAAS	"	Elfving et al. (1978)
"	"	0.6	None Noted	"	"	"	"	"	"
16 Manitoba soils	Crops	0.020-0.053	Background	"	Grains/ forage	Not applicable	"	"	Mills and Zwarich (1975)
"	"	(0.033)	"	"	"	"	"	"	"
11 Winnipeg Urban Soils	"	(0.029)	"	"	NR	"	"	"	"
126 Ontario soils	Field Crops	0.01-0.70 (0.07)	"	"	Small grains/ forage	"	FLAAS - CV	"	Frank et al. (1976)
Ontario Mineral Soils	Vegetables	0.02-0.78 (0.10)	"	"	Vegetables	"	"	"	"
Ontario Organic Soils	"	0.05-1.11 (0.41)	"	"	"	"	"	"	"

Table 5. Background total mercury levels in soils, continued.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Ontario Soils	Orchards	0.03-1.14 (0.29)	Background	Plant uptake	Apples	Not Applicable	FLAAS - CA	Field	Frank et al. (1976)
"	"	0.02-0.27 (0.07)	"	"	Cherries	"	"	"	"
"	"	0.02-0.18 (0.06)	"	"	Peaches	"	"	"	"
"	"	0.04-0.31 (0.10)	"	"	Grapes	"	"	"	"
Ontario Sandy Soils	Crops	0.01-0.70 (0.06)	"	"	NR	"	"	"	"
Ontario Loam Soils	"	0.02-0.78 (0.09)	"	"	NR	"	"	"	"
Ontario Clay Soils	"	0.03-0.46 (0.08)	"	"	NR	"	"	"	"
Alberta Brown Soil pH 7.2	"	0.024±0.007	" (Well drained)	"	Cultivated Crops	"	FLAAS	"	Dudas and Pawluk (1977
Alberta Black Soil pH 6.4	"	0.027±0.008	"	"	"	"	"	"	"
Alberta Gray Soil pH 6.5	"	0.024±0.005	"	"	"	"	"	"	"
Alberta Brown Soil pH 6.5	"	0.023±0.002	" (Poorly drained)	"	"	"	"	"	"
Alberta Black Soil pH 6.9	"	0.035±0.015	"	"	"	"	"	"	"
Alberta Gray Soil pH 7.4	"	0.037±0.011	"	"	"	"	"	"	"
Alberta Brown Soil pH 6.4	"	0.016±0.003	" (Solonetz)	"	"	"	"	"	"

Table 5. Background total mercury levels in soils, continued.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Berrien Co., MI									
pH (6.6)	Orchards	0.059-0.68 (0.23)	Background	Plant uptake	Apples	Maturity	FLAAS	Field	Shacklette(1980)
pH (5.4)	"	0.031-0.078 (0.044)	"	"	Pears	"	"	"	"
Wayne Co. NY									
pH (5.5)	Orchards	0.14-0.32 (0.20)	"	"	Apples	"	"	"	"
pH (5.5)	"	0.040-0.085 (0.059)	"	"	Peaches	"	"	"	"
pH (6.6)	"	0.047-0.096 (0.060)	"	"	Pears	"	"	"	"
pH (6.6)	"	0.04-2.6 (0.15)	"	"	Plum	"	"	"	"
Yakima Co. WA									
pH (6.6)	Orchards	0.018-0.11 (0.044)	"	"	Apples	"	"	"	"
pH (7.9)	"	0.01-0.16 (0.030)	"	"	European Grapes	"	"	"	"
pH (5.7)	"	0.032-0.063 (0.043)	"	"	Peaches	"	"	"	"
pH (6.3)	"	0.19-0.040 (0.29)	"	"	Pears	"	"	"	"
pH (6.8)	"	0.010-0.037 (0.025)	"	"	Plum	"	"	"	"
pH (7.1)	Field Crops	0.026-0.041 (0.032)	"	"	Potatoes	"	"	"	"
pH (6.6)	"	0.03-0.67 (0.046)	"	"	Tomatoes	"	"	"	"
Gloucester Co. NJ									
pH (5.5)	Orchards	0.01-0.13 (0.071)	"	"	Apples	"	"	"	"
Mesa Co. CO									
pH (7.8)	"	0.023-0.065 (0.041)	"	"	Apples	"	"	"	"
pH (7.7)	"	0.026-0.058 (0.040)	"	"	Peaches	"	"	"	"
pH (8.0)	"	0.019-0.20 (0.042)	"	"	Pears	"	"	"	"
pH (7.6)	"	0.029-0.062 (0.040)	"	"	Plum	"	"	"	"
pH (7.9)	Field Crops	0.029-0.046 (0.036)	"	"	Dry Beans	"	"	"	"
Twin Falls Co. ID									
pH (8.1)	"	0.03-0.046 (0.038)	"	"	Dry Beans	"	"	"	"
pH (8.2)	"	0.023-0.037 (0.031)	"	"	Potatoes	"	"	"	"
pH (8.3)	Vegetables	0.030-0.052 (0.037)	"	"	Snap Beans	"	"	"	"
pH (8.0)	"	0.024-0.043 (0.035)	"	"	Sweet Corn	"	"	"	"
San Joaquin Co. CA									
pH (6.4)	Orchards	0.01-0.039 (0.021)	"	"	European Grapes	"	"	"	"
pH (6.8)	"	0.030-0.043 (0.035)	"	"	Peaches	"	"	"	"
pH (7.0)	"	0.057-0.10 (0.073)	"	"	Pears	"	"	"	"
pH (7.5)	Vegetables	0.043-0.13 (0.082)	"	"	Cucumbers	"	"	"	"
pH (7.0)	Field Crops	0.016-0.035 (0.026)	"	"	Dry Beans	"	"	"	"
pH (8.5)	Vegetables	0.010-0.039 (0.026)	"	"	Tomatoes	"	"	"	"

Table 5. Background total mercury levels in soils, continued.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Alberta Black Soil pH 5.7	Crops	0.028±0.007	Background Poorly Drained	Plant uptake	Cultivated crops	Not Applicable	FLAAS	Field	Dudas and Pawluk (1977)
Alberta Gray Soil pH 6.2	"	0.041±0.029	"	"	"	"	"	"	"
Canadian Soils	Not Given	0.005-0.11(0.059)	"	NR	NR	"	NR	Field	McKeague et al (1979)
"	Uncultivated	0.06	"	NR	NR	"	AAS	"	McKeague and Wolynetz (1980)

Table 6. Elevated total mercury levels in soils.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Arenosa Fine Sand pH 4.7	Pasture	50	Toxic	Plant uptake	Bermuda grass	6 weeks	$HgCl_2$ Added	Field/soil pots	Weaver et al. (1984)
Weswood Silt Loam pH 7.7	Pasture	8	Reduced Plant Growth	" "	"	6 weeks	"	"	"
Houston Black clay pH 7.6	Pasture	50	Non Toxic	" "	"	6 weeks	"	"	"
Polluted Soils		0.24-0.40(0.36)	Not Noted	" "	Barley	N/A	INAA	Field	Singh and Steinnes (1976)
Hazelwood Silt Loam pH 5.1	Vegetables/Oats	20	Yields not stated	" "	Roots/ Leaves/ Grain/ Tubers/ Pods/Vines	Maturity	$HgCl_2$ Added	Greenhouse soil pots	John (1972)

al. 1979, McCarthy et al. 1970, Ratsch 1974, Shacklette 1970, Warren et al. 1966). Ratsch (1974) reported up to 11 ppm mercury in garden soils near the Ruston copper smelter in Tacoma, Washington. The hazard evaluation of excess total soil mercury is discussed in Section 3.2.

2.2.2 Mercury levels in vegetation

An increase in plant uptake of mercury with increased soil mercury levels has been demonstrated (Kabata-Pendias and Pendias 1984), however, plant translocation of soil mercury is low. Lead, chromium and mercury are so strongly held in root cells that very little is translocated to shoots of crop plants (Chaney 1984). Hogg et al. (1978) found fine roots of brome grass contained 43 to 102 ppm mercury, a level 2 to 4 times higher than levels found in primary or secondary roots. Similar results have been reported for rice, in which 1000 ppm was found in the roots and 0.5 ppm in the grain (Ishizuka and Tanaka 1962). Direct uptake of atmospheric mercury by alfalfa plant leaves has been suggested by Lindberg et al. 1979. Limited data suggest this mechanism is present in other species (Hitchcock and Zimmerman 1957). Although mercury translocation within plants is low, it is significant. John (1972) found elevated levels in edible portions of many vegetables grown on mercury ammended soil. This author reported radish tubers and spinach leaves accumulate the highest levels at 0.695 and 0.663 ppm respectively. Translocation of mercury to grains is apparently limited. Dudas and Pawluk (1977) found mercury levels in wheat, barley and oat straw to be 2 to 5 times higher than in the respective grains. Translocation of methylmercury from seed dressings to the first generation of wheat and peas has also been demonstrated (Kabata-Pendias and Pendias 1984, Lagervall and Westoo 1969, Smart 1968). The mercury concentration in some plant materials is apparently enhanced by lower temperatures and a reduced photoperiod. Hogg et al. (1978) found the mercury concentration of bromegrass increased as the photoperiod and temperatures decreased during the autumn months.

The toxicity of mercury to plants is caused by the affinity of mercury to sulfhydryl groups and the resulting disruption of metabolic processes (Kabata-Pendias and Pendias 1984). The high concentrations of mercury observed in roots inhibits potassium uptake (Kabata-Pendias and Pendias 1984). The symptoms of mercury poisoning in plants are usually manifested in stunting of seedling growth, decreased root mass, and inhibition of photosynthesis (Kabata-Pendias and Pendias 1984).

Background mercury levels in plants have been relatively well defined (Table 7). The typical range is from trace amounts (0.001 ppm) to about 0.200 ppm mercury. The highest mercury background level that has been reported in the literature reviewed is 0.237 for radishes (John 1972). Nearly all edible vegetative products contain <0.100 ppm mercury.

Considerable variation is apparent among different plant species in their uptake of mercury under elevated conditions (Table 8). Small grain cereal crops exhibit small but significant increases in grain mercury contents. John (1972) found the mercury content of oat grain to increase from the 0.009 ppm background level to 0.020 ppm in plants grown in soil with 20 ppm mercury content. Radish tubers, grown under the same conditions, increased from 0.013 to 0.663 ppm mercury, an increase of over 50 times. The limited amount of phytotoxic mercury plant concentration data derived from reviewed literature suggests a wide phytotoxic range occurs (from 0.2 ppm to 6.4 ppm), dependent on many factors including the mercury compound, the experimental design and the plant species. These problems and hazard level selection are discussed in Section 3.2.

2.3 Selenium Levels in Soils and Plants

Selenium is an element commonly found in trace quantities throughout the ecosystem. Selenium is not regarded as an essential element for most crop plants, but some indicator species have been shown to respond to selenium uptake (NRC 1976). This element has an important role in animal nutrition and disease. Selenium in livestock diets is required in minute amounts to

Table 7. Background mercury levels in plants.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Vegetation	Sweet Corn	0.003, 0.0046	Background	Plant uptake	Grain	NR	NR	NR	Kabata-Pendias and Pendias (1984)
Vegetation	Bean	0.003, 0.011	"	"	Pod	NR	NR	NR	"
Vegetation	Bean	0.017 WW, 0.07 WW	"	"	"	NR	NR	NR	"
Vegetation	Carrot	0.086, 0.0057	"	"	Root	NR	NR	NR	"
Vegetation	Lettuce	0.0083	"	"	Leaves	NR	NR	NR	"
Vegetation	Lettuce	<0.0006 WW	"	"	"	NR	NR	NR	"
Vegetation	Cabbage	0.0065	"	"	"	NR	NR	NR	"
Vegetation	Cabbage	0.010 WW	"	"	"	NR	NR	NR	Kitagishi and Yamane (1981)
Vegetation	Beet	0.003 WW	"	"	Root	NR	NR	NR	Kabata-Pendias and Pendias (1984)
Vegetation	Potatoes	0.047, <0.010	"	"	Tuber	NR	NR	NR	"
Vegetation	Potatoes	0.003 WW, 0.12 WW	"	"	"	NR	NR	NR	"
Vegetation	Onion	<0.010	"	"	Bulb	NR	NR	NR	"
Vegetation	Onion	0.007 WW	"	"	"	NR	NR	NR	"
Vegetation	Cucumber	0.001 WW, 0.011 WW	"	"	Unpeeled Fruit	NR	NR	NR	"
Vegetation	Tomato	0.0031, 0.034	"	"	Fruit	NR	NR	NR	"
Vegetation	Tomata	0.001 WW	"	"	"	NR	NR	NR	"
Vegetation	Apple	<0.010	"	"	"	NR	NR	NR	"
Vegetation	Apple	0.010 WW	"	"	"	NR	NR	NR	"
Vegetation	Orange	0.0026	"	"	"	NR	NR	NR	"
Vegetation	Lemon	0.043 WW	"	"	"	NR	NR	NR	"
Vegetation	Mushrooms	0.0035	"	"	Caps, Stalks	NR	NR	NR	"
Vegetation	Green/Yellow Vegetables	0.02 WW	"	"	Edible Parts	NR	NR	NR	Kitagishi and Yamane (1981)
Vegetation	Lettuce	0.031	"	"	Leaves	35 days	$HNO_3/HClO_4/$ FLAAS	Greenhouse/ Soil pots	John (1972)
Vegetation	Lettuce	0.112	"	"	Roots	"			"
Vegetation	Spinach	0.094	"	"	Leaves	55 days	"	"	"
Vegetation	Spinach	0.095	"	"	Roots	55 days	"	"	"
Vegetation	Broccoli	0.063	"	"	Leaves	60 days	"	"	"
Vegetation	Broccoli	0.171	"	"	Roots	60 days	"	"	"
Vegetation	Cauliflower	0.079	"	"	Leaves	70 days	"	"	"
Vegetation	Cauliflower	0.019	"	"	Roots	70 days	"	"	"
Vegetation	Peas	0.001	"	"	Seeds	95 days	"	"	"
Vegetation	Peas	0.005	"	"	Pods	95 days	"	"	"
Vegetation	Peas	0.110	"	"	Vines	95 days	"	"	"
Vegetation	Peas	0.011	"	"	Roots	95 days	"	"	"
Vegetation	Radishes	0.237	"	"	Tops	45 days	"	"	"
Vegetation	Radishes	0.013	"	"	Tubers	45 days	"	"	"
Vegetation	Carrots	0.024	"	"	Tops	130 days	"	"	"

Table 7. Background mercury levels in plants, continued.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Vegetation	Carrots	0.163	Background	Plant uptake	Roots	130 days	$HNO_3/HClO_4$/ FLAAS	Greenhouse/ Soil pots	John (1972)
Vegetation	Beans	<0.1	"	"	Edible portions	Maturity "	FLAAS "	Field "	Elfving et al (1978)
Vegetation	Cabbage	0.1	"	"	"	"	"	"	"
Vegetation	Carrots	0.1	"	"	"	"	"	"	"
Vegetation	Onions	0.2	"	"	"	"	"	"	"
Vegetation	Potatoes	0.1	"	"	"	"	"	"	"
Vegetation	Tomatoes	0.1	"	"	"	"	"	"	"
Vegetation	Corn	0.027	"	"	Leaves	"	"	"	Chaney (1973)
Vegetation	Corn	0.0052	"	"	Grain	"	"	"	"
Vegetation	Corn	0.0198	"	"	Leaves	"	"	"	"
Vegetation	Corn	0.002	"	"	Grain	"	"	"	"
Vegetation	Soybeans	0.062	"	"	Leaves	"	"	"	"
Vegetation	Soybeans	0.0028	"	"	Grain	"	"	"	"
Vegetation	Wheat/Barley	0.008-0.012	"	"	"	NR	NR	NR	Smart (1968)
Vegetation	Wheat	0.0053-0.0067	"	"	"	Maturity	FLAAS	Field	Dudas and
			(well drained)	"	"	"	"	"	Pawluk (1977)
Vegetation	Oats	0.0100	"	"	"	"	"	"	"
Vegetation	Barley	0.0060-0.0080	"	"	"	"	"	"	"
Vegetation	Wheat	0.0057-0.0063	"	"	"	"	"	"	"
			(poorly drained)						
Vegetation	Oats	0.0120	"	"	"	"	"	"	"
Vegetation	Barley	0.0063-0.0067	"	"	"	"	"	"	"
Vegetation	Barley (USA)	0.019	"	"	"	NR	NR	NR	Kabata-Pendias and
Vegetation	Oats (USA)	0.012	"	"	"	NR	NR	NR	Pendias (1984)
Vegetation	Wheat (USA)	0.014	"	"	"	NR	NR	NR	"
Vegetation	Wheat (USA)	0.010-0.016 WW	"	"	"	NR	NR	NR	"
Vegetation	Wheat (Japan)	0.02 WW	"	"	Soft Flour	NR	NR	NR	Kitagishi and Yamane (1981)
Vegetation	Oats	0.009	"	"	Grain	100 days	$HNO_3/HClO_4$/	Greenhouse/	John (1972)
Vegetation	Oats	0.107	"	"	Husks	"	FLAAS	Soil Pots	"
Vegetation	Oats	0.176	"	"	Leaves	"	"	"	"
Vegetation	Oats	0.011	"	"	Stalks	"	"	"	"
Vegetation	Oats	0.151	"	"	Roots	"	"	"	"
Vegetation	Millet	0.1	"	"	Above ground biomass	Maturity	FLAAS	Field	Elfving et al (1978)

Table 8. Elevated mercury levels in plants.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Vegetation	Leaf Lettuce	0.045	Not Noted	Soil Solution	Leaves	35 Days	$HNO_3/HClO_4$/FLAAS	Greenhouse/	John (1972)
Vegetation	"	0.387	" "	20 ugHg/g soil	Roots	35 Days	"	Soil Pots	"
Vegetation	Spinach	0.695	" "	"	Leaves	55 Days	"	"	"
Vegetation	"	1.067	" "	"	Roots	55 Days	"	"	"
Vegetation	Broccoli	0.029	" "	"	Leaves	60 Days	"	"	"
Vegetation	"	1.870	" "	"	Roots	60 Days	"	"	"
Vegetation	Cauliflower	0.061	" "	"	Leaves	70 Days	"	"	"
Vegetation	"	2.447	" "	"	Roots	70 Days	"	"	"
Vegetation	Peas	0.003	" "	"	Seeds	95 Days	"	"	"
Vegetation	"	0.042	" "	"	Pods	95 Days	"	"	"
Vegetation	"	0.085	" "	"	Vines	95 Days	"	"	"
Vegetation	"	1.415	" "	"	Roots	95 Days	"	"	"
Vegetation	Radishes	0.585	" "	"	Tops	45 Days	"	"	"
Vegetation	"	0.663	" "	"	Tubers	45 Days	"	"	"
Vegetation	Carrots	0.072	" "	"	Tops	130 Days	"	"	"
Vegetation	"	0.039	" "	"	Tubers	130 Days	"	"	"
Vegetation	"	1.058	" "	"	Roots	130 Days	"	"	"
Vegetation	Tomato	0.6 WW	9.9% YR	MMH Nut/	Terminal	2 Days	Mercury Analyzer	Greenhouse/	Haney and
Vegetation	"	1.5 WW	27% YR	Solution	Foliage	2 Days	"	pot culture	Lipsey (1973)
Vegetation	"	2.3 WW	72.8% YR	"	"	2 Days	"	"	"
Vegetation	"	3.4 WW	90.9% YR	"	"	2 Days	"	"	"
Vegetation	"	1.0 WW	88.9 YR	"	"	10 Days	"	"	"
Vegetation	"	0.7 WW	68.8% YR	"	"	10 Days	"	"	"
Vegetation	"	0.8 WW	11.0 YR	"	"	10 Days	"	"	"
Vegetation	"	0.2 WW	0.0% YR	"	"	10 Days	"	"	"
Vegetation	Barley	2-5 (3)	10% YR	$HgCl_2$ Solution	Leaves/ Shoots	5 leaf/ stage	XRFL	Greenhouse/ sand culture	Davis et al. (1978)
Vegetation	Bermuda grass	2.9	Not Toxic	Arenosa fine	Leaves	6 weeks	$HNO_3/HClO_4$/FLAAS	Field/Soil	Weaver et al.
Vegetation	Bermuda grass	6.4	Toxic	sand	Leaves	6 weeks	"	pots	(1984)
Vegetation	Bermuda grass	0.2	Sig. wt. reduction	Westwood silt loam	Leaves	6 weeks	"		"
Vegetation	Alfalfa	2.3	Nontoxic	Almaden soil	Above/	16 weeks	$HNO_3/HClO_4/K_2CrO_7$	Greenhouse/	Lindberg et
Vegetation	Alfalfa	1.4	Nontoxic	Control soil	ground Biomass	16 weeks	AAS	soil pots	al. (1979)
Vegetation	Alfalfa	9.8	Uncertain	Almaden soil	Roots	16 weeks	"	"	"
Vegetation	Oats	0.020	Not Noted	Soil solution/	Grain	100 Days	$HNO_3/HClO_4$/FLASS	"	John (1972)
Vegetation	Oats	0.266	" "	20 ugHg/g soil	Husks	100 Days	"	"	"
Vegetation	Oats	0.199	" "	"	Leaves	100 Days	"	"	"
Vegetation	Oats	0.026	" "	"	Stalks	100 Days	"	"	"
Vegetation	Oats	0.426	" "	"	Roots	100 Days	"	"	"
Vegetation	Rice	0.5	Toxic	Plant uptake	Stem/ Leaf	NR	NR	Solution Culture	Ishizuka and Tanaka (1962)
Vegetation	Rice	1000	Toxic	" "	Roots	NR	NR	"	"

prevent disorders such as white muscle disease. While excessive levels of selenium in forage are known to cause selenium poisoning or "alkali disease".

The factors affecting selenium availability and uptake by plants include the form of selenium in soil, soil type, soil pH, climate, presence of other elements and plant species (Whanger 1974). The inorganic phases of selenium occur as elemental selenium, as metal selenide, as a substitute in sulfides, as selenite and as selenate. Organic selenium occurs in soil as a result of partially decayed seleniferous vegetation. The most plant available forms are selenate and organic selenium (Gough, et al. 1979). The slightly mobile selenides and selenium sulfides dominate in acidic, poorly drained soils with high organic matter levels. Selenites, which are moderately available to plants, exist in well drained, neutral pH soils. Alkaline, well oxidized soils may contain appreciable levels of the soluble and readily available selenate form (Allaway 1968b, Lakin and Davidson 1967, Paasikallio 1981). The presence of other elements in the soil which are chemically similar to selenium, particularly sulfur, will result in the decrease in selenium uptake by the plant (Whanger 1974). Plant uptake of selenium is also dependent on the plant species involved. Most agricultural species accumulate only a few ppm while indicator species such as those in the genus Astragalus can accumulate up to 10,000 ppm (Rosenfeld and Beath 1964).

The following sections present selenium data for soils and plants reported in the reviewed literature.

2.3.1 Total selenium levels in soils

Selenium is found throughout the lithosphere at concentrations seldom exceeding 0.05 ppm (Kabata-Pendias and Pendias 1984). A world wide average for total selenium in surface soils is 0.40 ppm. A review of the literature suggests that the background level of total selenium in soils of the United States varies from 0.005 to 4.0 ppm. Tables 9 and 10 summarize the

Table 9. Background total selenium levels in soils.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Soil, Colorado, Surface horizon	Cultivated and Uncultivated	0.1-1.4 (0.23)	Background	Plant uptake	NR	NR	XRFL	Field (168 samples)	Connor and Shacklette (1975)
Soil, Eastern U.S., B horizon	"	0.1-1.4 (0.39)	"	"	NR	NR	XRFL	Field (1000 samples)	"
Soil, Western U.S., B horizon	"	0.1-4.3 (0.25)	"	"	NR	NR	XRFL	Field (1000 samples)	"
Soils, Western U.S.	"	0.1-2.0	"	"	NR	NR	NR	Field	Swaine (1955)
Soils, Massachusetts	Vegetables	2.4-5.1 (3.5)	"	"	NR	NR	INAA/RNAA	Field	Laul et al. (1977)
Soils, Wash., Surface	Vegetables	1.7	"	"	NR	NR	"	Field	"
Soils, Ontario, Clay, pH 6.3	Agricultural	0.209	"	"	NR	NR	NR	Field	Levesque (1974)
Loam, pH 6.8	"	0.321	"	"	NR	NR	NR	"	"
Clay, PH 6.7	"	0.395	"	"	NR	NR	NR	"	"
Clay, pH 6.3	"	0.744	"	"	NR	NR	NR	"	"
Clay, pH 4.5	"	0.530	"	"	NR	NR	NR	"	"
Clay, pH 5.2	"	0.460	"	"	NR	NR	NR	"	"
Loam, pH 7.0	"	0.450	"	"	NR	NR	NR	"	"
Loam, pH 7.2	"	0.425	"	"	NR	NR	NR	"	"
Loam, pH 7.1	"	0.652	"	"	NR	NR	NR	"	"
Loam, pH 6.0	"	0.197	"	"	NR	NR	NR	"	"
Soils, U.S.	NR	0.005-4.0	"	"	NR	NR	NR	Field	Kabata-Pendias and Pendias (1984)
Soils, World-wide	NR	0.005-4.0 (0.40)	"	"	NR	NR	NR	"	"
Soils, Helena Valley, pH 8.0	NR	0.07	"	"	NR	NR	Acid digestion, AAS analysis	"	EPA (1986)

Table 9. Background total selenium levels in soils, continued.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Soil, Sandy Ont., Canada	Agricultural	0.10-1.32 (0.27)	Background	"	NR	NR	H_2SO_4/HNO_3 Digestion AAS	Field	Frank et al. (1979)
Soil, Loam Ont., Canada	Agricultural	0.13-1.67 (0.38)	Background	Plant uptake	NR	NR	H_2SO_4/HNO_3 Digestion AAS	Field	Frank et al. (1979)
Soil, Clay Ont., Canada	"	0.16-1.43 (0.48)	"	"	NR	NR	"	"	"
Soil, Organic Ont., Canada	"	0.10-0.75 (0.34)	"	"	NR	NR	"	"	"
Soil, Muck Canada, Surface	Garden	1.3	"	"	Vegetables	NR	IPAA	Field	Chattopadhyay and Jervis (1974)
0-7.5 cm	"	1.22	"	"	"	NR	IPAA	"	
7.5-15 cm	"	0.81	"	"	"	NR	IPAA	"	"
15-22.5 cm	"	0.62	"	"	"	NR	IPAA	"	"
22.5-30 cm	"	1.05	"	"	"	NR	IPAA	"	"
30-37.5 cm	"	0.91	"	"	"	NR	IPAA	"	"
37.5-45 cm	"	0.53	"	"	"	NR	IPAA	"	"
Soil, Missouri, 0-15 cm	Cultivation	0.2-1.5 (0.45)	"	"	Corn	Maturity	XRFL	Field	Connor and Shacklette (1975)
"	"	0.1-1.4 (0.51)	"	"	Soybeans	Maturity	"	"	
"	"	0.1-1.5 (0.44)	"	"	Pasture	Maturity	"	"	"
Soil, Missouri, Surface horizon	"	0.1-2.7 (0.28)	"	"	NR	NR	"	Field (300 samples)	"
Soil, Missouri B horizon	Native	0.1-3.4 (0.43)	"	"	NR	NR	"	Field	"
Soils, Canada 0-15 cm, pH 5.9	Alfalfa	0.31	Background	Plant uptake	Plant tops	Bud stage	Flouro-metrically	Field	Van Ryswyk et al. (1976)
65-87 cm, pH 7.1	"	0.22	"	"	"	"	"	"	"
0-15 cm, pH 7.2	"	0.24	"	"	"	"	"	"	"
81-103 cm, pH 7.5	"	0.29	"	"	"	"	"	"	"
Soils, Canada	NR	0.03-2 (0.26)	Background	Plant uptake	NR	NR	Flouro-metrically	Field (173 samples)	McKeague and Wolynetz (1980)

Table 9. Background total selenium levels in soils, continued.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Soil, Berrier Co. MI pH (6.6)	Orchard	<Ø.1-Ø.61 (Ø.Ø95)	Background	Plant Uptake	Apples	Maturity	XRFL	Field	Shacklette (198Ø)
Soil, Wayne Co. NY pH (5.5)	"	<Ø.1 "	"	"	Apples	"	"	"	"
Soil, Gloucester Co. NJ pH (5.5)	"	<Ø.1 "	"	"	Apples	"	"	"	"
Soil, Yakima Co. WA pH (6.6)	"	<Ø.1-Ø.34 (Ø.11)	"	"	Apples	"	"	"	"
Soil, Mesa Co., CO pH (7.8)	"	<Ø.1-Ø.4 (Ø.13)	"	"	Apples	"	"	"	"
Soil, Twin Falls Co. ID pH (8.2)	Vegetables	<Ø.1-(Ø.21)	"	"	Potatoes	"	"	"	

Table 10. Elevated total selenium levels in soils.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Soil, Surface	NR	10	"Phytotoxically excessive"	NR	NR	NR	NR	NR	EL-Bassan and Tietjen (1977)
"	"	5	"	"	"	"	"	"	Linzon (1978)
"	"	10	"	"	"	"	"	"	Kabata-Pendias (1979)
"	"	10	"	"	"	"	"	"	Kloke (1979)
Soils	Buckwheat	76.6	"Plants died"	64 ppm Se added to soil	NR	Maturity	Colorimetrically	Field plot	Martin (1936)
Soils	Buckwheat	10.5-39.6	"Growth retarded"	8-32 ppm Se added to soil	"	"	"	" "	"
Soils, Clay loam	Wheat	30	"Rapid yellowing and death"	Plant uptake	"	NR	NR	Greenhouse	Hurd-Karrer (1934)

literature pertaining to background and elevated levels of selenium in soils.

Few articles have reported phytotoxic levels of selenium in soils. Much of the concern associated with excess selenium stems from the toxicity of seleniferous plants to grazing animals. Seleniferous soils (>5.0 ppm total selenium) often support vegetation that is toxic to animals, however, these soils are generally not toxic to the plants growing naturally on them (NRC 1976). Kabata-Pendias and Pendias (1984) reviewed literature (not available to the present authors) that reported total soil selenium concentrations of 5 to 10 ppm as being phytotoxically excessive. Hurd-Karrer (1934) reported the death of wheat seedlings when soil selenium concentrations reached 30 ppm in greenhouse studies. The growth of buckwheat plants has been retarded at soil selenium levels of 10.5 to 39.6 ppm (Martin 1936). Death of these buckwheat plants occurred at a total soil selenium concentration of 76.6 ppm.

2.3.2 Selenium levels in plants

Rosenfeld and Beath (1964) proposed the classification of plants based on their ability to accumulate selenium and their potential toxicity to livestock. Group 1 plants were termed primary indicator or accumulator species which could absorb from 100 to 10,000 ppm. Most notable of this group were the *Astragalus* species. Group 2 plants were secondary selenium accumulators that rarely contained more than a few hundred ppm selenium. Most cultivated crops, grains and native grasses were classified as Group 3 plants. These species rarely accumulated more than 30 ppm total selenium. Tables 11 and 12 summarize background and elevated levels of selenium in plants reported in reviewed literature.

Vegetation containing greater than 2.0 ppm total selenium can be toxic to animals consuming it (NRC 1980). However, the same vegetation could contain selenium levels in great excess of this before experiencing phytotoxic symptoms.

An appreciable amount of literature exists on selenium levels in agricultural and range plants (non-accumulator species) and indicates that background concentrations usually range from 0 to 84 ppm (Table 11). While selenium is probably not essential for vegetative growth, the soluble forms of selenium are readily absorbed by plant roots (Kabata-Pendias and Pendias 1984). Because of the various solubilities and chemical forms of selenium, it is difficult to correlate the amount of total selenium in soils with the tissue concentration of plants.

Little documentation has been found concerning the determination of phytotoxic selenium levels in plant tissue. Martin (1936) reported growth reduction in buckwheat plants containing 35 to 124 ppm and death of plants containing 127 ppm selenium. A reduction in growth occurred in tomatoes with 191 ppm selenium (Yopp et al. 1974). Soltanpour and Workman (1980) concluded that 360 ppm selenium in the tops of alfalfa was responsible for very low yields while 1000 ppm was highly toxic. Selenium hazard levels for soils and plants are discussed in Section 3.3.

2.4 Silver Levels in Soils and Plants

Naturally occurring silver is found in minute quantities throughout the oceans, lithosphere, soils, plants and animals. Silver is similar to copper in its geochemical characteristics and exists as simple cations (Ag^+, Ag^{2+}, AgO^+) and complexed anions [AgO^-, $Ag(S_2O_3)_2^{3-}$, $Ag(SO_4)_2^{3-}$] (Kabata-Pendias and Pendias 1984). Silver is absorbed and complexed by organic matter and is apparently immobile at pH >4 (Kabata-Pendias and Pendias 1984). The availability of silver to plants is low due to the very low solubility of most of its compounds. Silver has not been proven to be essential for plant life (Vanselow 1965). The soluble fraction is extremely toxic, particularly to microorganisms and fish (Cooper and Jolly 1970). Silver, however, is relatively harmless to higher animals, including man. Silver data for soils and plants are presented in the following sections.

Table 11. Background selenium levels in plants.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Vegetation, Missouri	Corn	0.01-0.5 (0.06)	Background	Plant uptake	Grain	Maturity	2-3 Diamino-naphthalene	Field	Connor and Shacklette (1975)
"	Soybean	0.04-1.25 (0.11)	"	"	Seeds	Maturity	"	"	"
"	Buckbrush	0.02-0.08 (0.03)	"	"	NR	NR	"	"	"
"	Cedar	0.01-0.04 (0.02)	"	"	NR	NR	"	"	"
"	Shagbark Hickory	0.02-0.04 (0.02)	"	"	NR	NR	"	"	"
"	Post Oak	0.01-0.04 (0.02)	"	"	NR	NR	"	"	"
"	White Oak	0.01-0.04 (0.019)	"	"	NR	NR	"	"	"
"	Willow Oak	0.01-0.3 (0.032)	"	"	NR	NR	"	"	"
"	Shortleaf Pine	0.02-0.2 (0.062)	"	"	NR	NR	"	"	"
"	Smooth Sumac	0.01-0.25 (0.02)	"	"	NR	NR	"	"	"
"	Sweetgum	0.01-0.4 (0.065)	"	"	NR	NR	"	"	"
Vegetation	Sagebrush	0.08-4.8 (0.42)	"	"	NR	NR	"	"	"
Vegetation, Washington	Cheatgrass	<0.03	Background	Plant uptake	Interior portions	NR	INAA and RNAA	Field	Laul et al. (1977)
Vegetation, Worldwide	Grasses	.001-.21	"	"	NR	NR	NR	NR	Kabata-Pendias and Pendias (1984)
"	Clovers or alfalfa	.005-.88	"	"	NR	NR	NR	NR	"
"	Hay or fodder	.002-.87	"	"	NR	NR	NR	NR	"
Vegetation, U.S.	Grasses	.01-.04	"	"	NR	NR	NR	NR	"
"	Clover or alfalfa	.03-.88	Background	Plant uptake	NR	NR	NR	NR	Kabata-Pendias and Pendias (1984)

Table 11. Background selenium levels in plants, continued.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Vegetation, U.S.	Hay or fodder	.03-.36	"	"	NR	NR	NR	NR	"
Vegetation, Northwest U.S	Rangelands	0.01-0.78	"	"	Plant tops	NR	Flourometrically	Field (94 samples)	Carter et al. (1970)
"	Forage and Hay crops	0.0-1.24	"	"	"	NR	"	Field (361 samples)	"
Vegetation, Western U.S.	Wheat	0.01-25.0	"	"	NR	NR	NR	Field (710 samples)	Rosenfeld and Beath (1964)
"	Wheat	0.01-30.0	"	"	Grain	NR	NR	Field (176 samples)	"
Vegetation, South Dakota	Native grass	0.0-84.0	"	"	NR	NR	NR	Field (294 samples)	"
Vegetation, South Central British Columbia	6 Native Species	<1.0	"	"	Grazing stock	NR	AAS	Field (294 samples)	Fletcher and Brink (1969)
Vegetation	Lettuce	0.002 WW	Background	Plant uptake	NR	NR	Acid digestion	NR	Wolnik et al. (1983)
	Peanuts	0.057 WW	"	"	NR	NR	FLAAS analysis	NR	"
	Potatoes	0.003 WW	"	"	NR	NR	"	NR	"
	Soybeans	0.19 WW	"	"	NR	NR	"	NR	"
	Sweet Corn	0.006 WW	"	"	NR	NR	"	NR	"
	Wheat	0.37 WW	"	"	NR	NR	"	NR	"
Vegetation, Canada	Timothy	0.005-0.023	"	"	NR	NR	NR	Field	Gupta and Winter (1975)
"	Red clover	0.004-0.031	"	"	NR	NR	NR	Field	
"	Oats	0.004-0.043	"	"	Kernal	NR	NR	Field	"
"	Barley	0.006-0.040	"	"	Kernal	NR	NR	Field	"
Vegetation, Massachusetts	Corn	<0.03	Background	Plant uptake	Interior portions	NR	INAA and RNAA	Field	Laul et al. (1977)
"	Potatoes	<0.03	"	"		NR	"	"	
"	Peas	<0.03	"	"	"	NR	"	"	"
"	Squash	<0.03	"	"	"	NR	"	"	"

Table 12. Elevated selenium levels in plants.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Vegetation, Illinois	Wheat	380	"No injury to plant"	NR	NR	NR	NR	NR	Yopp et al. (1974)
Vegetation, Illinois	Tomato	191	"Growth reduction"	NR	NR	NR	NR	NR	"
Vegetation	Buckwheat	127	"Plants died"	64 ppm Se added to soil	NR	Maturity	Colorimetrically	NR	Martin (1936)
Vegetation	Buckwheat	35-124	"Growth retarded"	8-32 ppm Se added to soil	NR	"	"	NR	"
Vegetation	NR	5-30	"Excessive or toxic"	NR	Leaf tissue	"	NR	NR	Kabata-Pendias and Pendias (1984)
Vegetation	Alfalfa	360	"Produced very low yields"	NR	Plant top	NR	Hot water extract ICP analysis	Greenhouse	Soltanpour and Workman (1980)
Vegetation	Alfalfa	1000	"Highly toxic"	NR	"	NR	"	"	"
Central Oregon	Alfalfa	0.13-0.34	No effect	Na_2SeO_3 added to soil	Plant top	1 year	Allaway and Carey (1964)	Field	Allaway et al. (1966)

2.4.1 Total silver levels in soils

Silver is an element found universally in soils (Vanselow 1965). Literature reviewed by Smith and Carson (1977b) shows that background levels of silver in soils range from 0.1 to 5.0 ppm. Reported background silver levels in the United States indicate total silver concentrations in soils seldom exceed 0.5 ppm (Connor and Shacklette 1975). No literature has been found on extractable levels of silver in undisturbed soils. Tables 13 and 14 summarize the background and elevated silver levels in soils found in the reviewed literature.

Few studies have determined phytotoxic levels of silver in soils. Concern regarding silver pollution of soils has emerged recently due to increased use of silver iodide as a nucleating agent for promoting precipitation (cloud seeding). Research has shown that typical aerial fallout levels of silver from cloud seeding (10^{-7} to 3×10^{-7} ppm) poses no immediate threat to the soil resource (Cooper and Jolly 1970). Aerial deposition of silver near a silver mine and treatment plant in New Zealand resulted in average soil silver concentrations (1.7 ppm) being significantly greater than background (0.2 ppm) concentrations (Ward et al. 1977). These elevated silver levels decreased with distance from the treatment plant. The only soil phytotoxic criteria found in the reviewed literature was that of Linzon (1978) who reported 2 ppm total soil silver was phytotoxically excessive.

2.4.2 Silver levels in plants

A study of 35 plant species, representing the major vascular plant groups, revealed background plant tissue silver concentrations ranged from 0.01 to 16.0 ppm (Horovitz et al. 1974). These authors noted higher silver content in some fungi and bryophytes and lower values in angiosperms and gymnosperms. A large amount of literature published on silver concentrations in plants indicate that background concentrations usually range from 0 to 1.0 ppm (Table 15). Shacklette (1980) reported less than 1 ppm (ash weight basis) for most fruits and vegetables

Table 13. Background total silver levels in soils.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Soil, Missouri (0-15 cm)	Cultivated	<0.5-3 (<0.5)	Background	Plant uptake	NR	NR	6-step ES	Field (1400 samples)	Connor and Shacklette (1975)
Soil, Missouri B-horizon	Oak-Hickory Forest	<0.5-3 (<0.5)	"	"	NR	NR	"	Field (300 samples)	"
Soil, Colorado (0-15 cm)	Cultivated and Uncultivated	<0.5-1.5 (<0.5)	"	"	NR	NR	"	Field (168 samples)	"
Soil, Western U.S. (20 cm)	Native Vegetation	<0.5-5 (<0.5)	"	"	NR	NR	"	Field (1000 samples)	"
Soils, Ontario Canada (0-15 cm)	Croplands	0.04-1.81 (0.44)	"	"	NR	NR	HNO_3 Digestion AAS analysis	Field (228 samples)	Frank et al. (1979)
Soils, Worldwide	Cultivated and Native	<0.01-5.0	"	"	NR	NR	Spectrographically	Field	Swaine (1955)
Soils, Helena Valley pH 8.0	"	0.25	"	"	NR	NR	Acid digestion, AAS analysis	Field	EPA (1986)
Soils, Surface Muck, Canada	Garden	0.89	"	"	Vegetables	NR	IPAA	Field	Chattopadhyay and Jervis (1974)
0-7.5 cm	"	0.68	"	"	"	NR	"	"	"
7.5-15 cm	"	0.52	"	"	"	NR	"	"	"
15-22.5 cm	"	0.40	"	"	"	NR	"	"	
Soils, Scotland	NR	≤2.0	"	"	NR	NR	NR	Field	Vanselow (1965)
Soils, Missouri	Agricultural	0.7	"	"	NR	NR	NR	Field	"
Soils, California	NR	0.2-0.7	"	"	NR	NR	NR	Field	"
Soils, surface New Zealand	Native	0.21	"	"	NR	NR	Acid disgestion, AAS analysis	Field	Ward et al. (1977)
Aberdeenshire UK	NR	0.29-0.50	"	"	NR	NR	SSMS	Field	Ure and Bacon (1978)
Tubingen Univ Germany	Botanical Garden	0.08-0.09	"	"	Juniperus Communis-Ephedragerardiana	NR	RNAA	Field	Horovitz et al. (1974)

Table 14. Elevated total silver levels in soils.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Soils, surface	NR	2.0	"Phytotoxically excessive"	Plant uptake	NR	NR	NR	NR	Linzon (1978)
Soils, surface New Zealand	Native	0.75-3.3(1.7)	"Significantly higher than background"	Aerial fallout	NR	NR	Acid digestion, AAS analysis	Field	Ward et al. (1977)

Table 15. Background silver levels in plants.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Vegetation	Vascular plants	5.0	Background	Uptake from soil	Plant	NR	NR	NR	Shacklette (1965)
Vegetation	Gymnosperms	0.07	"	"	"	NR	NR	NR	Bowen (1966)
Vegetation British Columbia	Gymnosperms	0-1.4	"	"	"	NR	Fire assay	Field	Warren and Delavault (1950)
Vegetation, U.S.	Angiosperms	0.06	"	"	Plant tops	NR	ES	"	Cannon et al. (1968)
Vegetation British Columbia	Angiosperms	0-.28	"	"	Plant	NR	Fire assay	"	Warren and Delavault (1950)
Vegetation	Grains and cereals	0.9	"	"	"	NR	NR	NR	Browning (1961)
"	Generalized	0.5	"	"	Leaf tissue	Maturity	NR	NR	Kabata-Pendias and Pendias (1984)
Vegetation, Georgia	Snap Bean	<0.5	"	"	Edible portions	Maturity	Plant ash, 6-step ES	Field	Connor and Shacklette (1975)
Vegetation	Cabbage	<0.5	"	"	"	Maturity	"	"	"
"	Tomato	<0.5	"	"	"	Maturity	"	"	"
"	Alfalfa	0.1-0.5	"	"	Tops	NR	NR	Field	Vanselow (1965)
"	Bur clover	0.2-0.5	"	"	"	NR	NR	"	"
"	Ladino clover	0.4-0.6	"	"	"	NR	NR	"	"
"	Grasses	0.1-0.4	"	"	"	NR	NR	"	"
"	Wheat	0.4	"	"	Whole grain	Maturity	NR	"	"
Vegetation Powder Ridge Basin	Big Sagebrush	<1.0	Background Geometric mean	"	Plant	NR	Plant ash, ES	"	Connor et al. (1976)

Table 15. Background silver levels in plants, continued.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Vegetation, New Zealand	Tawa (tree)	0.22	Background	Uptake from soil	Washed leaves	NR	Ashed, AAS	Field	Ward et al. (1977)
"	"	0.24	"	"	Unwashed leaves	NR	"	"	"
"	"	0.20	"	"	Washed twigs	NR	"	"	"
"	Perennial ryegrass	0.06	"	"	Roots	NR	"	"	"
"	"	0.08	"	"	Leaves	NR	"	"	"
"	White clover	0.08	"	"	Roots	NR	"	"	"
"	"	0.10	"	"	Leaves	NR	"	"	"
"	Annual bluegrass	0.06	"	"	Roots	NR	"	"	"
"	"	0.07	"	"	Leaves	NR	"	"	"
"	Cocksfoot	0.10	"	"	Roots	NR	"	"	"
"	"	0.10	"	"	Leaves	NR	"	"	"
"	Yorkshire fog	0.06	"	"	Roots	NR	"	"	"
"	"	0.08	"	"	Leaves	NR	"	"	"
"	Flatweeds	0.12	"	"	Roots	NR	"	"	"
"	"	0.14	"	"	Leaves	NR	"	"	"
"	Birdsfoot treefoil	0.08	"	"	Roots	NR	"	"	"
"	"	0.08	"	"	Leaves	NR	"	"	"

Table 15. Background silver levels in plants, continued.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Commercial Farms USA (1980)	Vineyard	<0.045	Background	Plant Uptake	American Grapes - Fruit	NR	ES	Field	Shacklette (1980)
"	Orchard	<0.016-0.032	"	"	Apples-Fruit	NR	ES	Field	"
"	Vineyard	<0.027	"	"	European Grapes - Fruit	NR	ES	Field	"
"	Orchard	<0.067-0.134	"	"	Peaches-Fruit	NR	ES	Field	"
"	"	<0.021	"	"	Pears-Fruit	NR	ES	Field	"
"	"	<0.048-0.144	"	"	Plums-Fruit	NR	ES	Field	"
"	Vegetables	<0.093	"	"	Cabbage-Heads	NR	ES	Field	"
"	"	<0.071	"	"	Carrots-Roots	NR	ES	Field	"
"	"	<0.100	"	"	Cucumbers-Fruit	NR	ES	Field	"
"	"	<0.039-0.117	"	"	Dry Beans	NR	ES	Field	"
"	"	<0.140-0.28	"	"	Lettuce-Heads	NR	ES	Field	"
"	"	<0.042-0.042	"	"	Potatoes-Tubers	NR	ES	Field	"
"	"	<0.070	"	"	Snap Beans-Pops	NR	ES	Field	"
"	"	<0.026	"	"	Sweet Corn-Grains	NR	ES	Field	"
"	"	<0.120	"	"	Tomatoes-Fruit	NR	ES	Field	"
"	"	<0.100	"	"	Asparagus-Shoots	NR	ES	Field	"
"	"	<0.098	"	"	Cantaloupes-Fruit	NR	ES	Field	"
"	"	<0.200	"	"	Chinese Cabbage - Leaves	NR	ES	Field	"
"	"	<0.074	"	"	Eggplant-Fruit	NR	ES	Field	"
"	"	<0.220	"	"	Endive-Leaves	NR	ES	Field	"
"	"	<0.042	"	"	Onions-Bulbs	NR	ES	Field	"
"	"	<0.190	"	"	Parsley-Leaves	NR	ES	Field	"
"	"	<0.084	"	"	Fresh Peppers - Fruit	NR	ES	Field	"

tested (25 species). The maximum silver concentration was found in fresh lettuce (0.28 ppm DW). The amount of silver taken up by plants is related to the amount of the metal in the soil (Kabata-Pendias and Pendias 1984). Therefore, elevated levels of silver could accumulate in plants growing in soils enriched with silver due to aerial deposition from smelting. Tables 15 and 16 present background and elevated data for silver levels in plants.

Little research has been conducted on the determination of excessive levels of silver in plant tissue. Ward et al. (1977) reported that a mean of 1.2 ppm in roots and 1.8 ppm in leaves of pasture species were significantly higher than background levels. A 10% yield reduction occurred in spring barley with 4 ppm silver in plant tops (Davis et al. 1978). Bush bean yields were reduced with 1760 ppm silver in roots, 5.1 ppm in stems and 5.8 ppm in plant tops (Wallace et al. 1977b). Silver hazard levels for plants and soils are discussed in Section 3.4.

2.5 Thallium Levels in Soils and Plants

Thallium is a rare element that is found in trace quantities in most soils and geological materials. Thallium exists in both mono(Tl^{+1}) and trivalent (Tl^{+3}) states and compounds of both forms are highly toxic (Logan et al. 1983). Monovalent thallium forms "sparingly" soluble compounds similar to the heavy metals copper, silver, gold, mercury and lead. The anion of these compounds include sulfides, iodides, chlorides and chromates (Smith and Carson 1977a). Trivalent thallium is usually found only in very acid environments (Smith and Carson 1977a). Thallium is geochemically similar to the alkali metals (potassium, rubidium and cesium) and is found as an isomorphic substitution in potassium feldspars (orthoclase, microcline, sanidine), micas and potassium feldspathoids (leucite) (Wedephol 1978). The element is also found in many metalic sulfide ores including sphalerite, pyrite and galena (Smith and Carson 1977a). Thallium is usually disseminated in low temperature hydrothermal deposits of antimony, mercury, lead and zinc and ores high in arsenic content have been found to be enriched in thallium (Velikii et

Table 16. Elevated silver levels in plants.

Medium	Use	Level (ppm DW) means in ( )	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Vegetation	Bush Bean	1.0	"No toxicity"	Nutrient Solution 0 ppm Ag	Roots	13 Days	Emission Spectrography	Greenhouse	Wallace et al. (1977b)
Vegetation	"	0.3	"	"	Stems	"	"	"	"
Vegetation	"	0.2	"	"	Leaves	"	"	"	"
Vegetation	"	83	"	Nutrient Solution 0.108 ppm Ag	Roots	"	"	"	"
Vegetation	"	0.8	"	"	Stems	"	"	"	"
Vegetation	"	1.0	"	"	Leaves	"	"	"	"
Vegetation	"	1760	"Yields greatly decreased"	Nutient Solution 1.08 ppm Ag	Roots	"	"	"	"
Vegetation	"	5.1	"	"	Stems	"	"	"	"
Vegetation	"	5.8	"	"	Leaves	"	"	"	"
Vegetation	Spring Barley	4.0	"10% yield reduction"	Sand Culture Nutrient Solution	Plant tops	27 Days	Tri-acid digestion Colorimetric analysis	"	Davis et al. (1978)
Vegetation New Zealand	Pasture species	1.2	"Significantly higher than background"	Plant uptake Aerial fallout	Roots	NR	Ashed, Atomic Absorption	Field	Ward et al. (1977)
Vegetation New Zealand	"	1.8	"	"	Leaves	NR	"	"	"
Vegetation	NR	5-10	"Excessive or Toxic"	NR	Leaf tissue	Maturity	NR	NR	Kabata-Pendias and Pendias (1984)

al. 1968). Many gold ores are commonly enriched in thallium (Zimmerley 1947). Thallium is commonly present in coal at approximately 0.7 ppm, probably as sulfide inclusions (Smith and Carson 1977a).

Thallium has been used in the past as an insecticide and rodenticide but has been banned from these products used in the United States since 1972 (Smith and Carson 1977a). Carlson et al. (1975) have reported thallium salts were most phytotoxic of thallium, lead, cadmium and nickel salts that were tested on hydroponically grown corn and sunflowers.

Thallium is released to the environment from combustion of coal and from smelting operations. It is used primarily in electrical component manufacturing (Smith and Carson 1977a). An assessment of anthropogenic deposition of thallium suggested little or no increase over present levels is expected in the future (Galloway et al. 1982), but local areas may be impacted by thallium pollution (Scholl and Metzger 1981).

2.5.1 Total thallium levels in soils

Few reports have been published on the characteristics of thallium in soils. Thallium is easily mobilized and transported together with alkaline metals (Kabata-Pendias and Pendias 1984) and is apparently readily available to plants (Scholl and Metzger 1981, Hoffman et al. 1982). Thallium is immobilized in soils through fixation by clays and manganese or iron oxides, and can be sorbed by organic matter (Kabata-Pendias and Pendias 1984). Thallium may also be removed from the soil solution by base exchange (McCool 1933).

Thallium occurs in trace amounts in most rocks but is found in higher concentrations in acid rocks (granites, gneisses) than in mafic or ultra mafic rocks (basalts, gabbros, dunites, peridotites and pyroxenites) (Bohmer and Pille 1977, Kabata-Pendias and Pendias 1984, Smith and Carson 1977a). Background levels of thallium in igneous rocks range from 0.05 to 2.3 ppm. Thallium is found at higher concentrations in fine grained (claystone/shale) sedimentary rocks as compared to coarse grained rocks. Typical thallium levels in shales and sandstones have been reported as 0.5 to 2.0 ppm and 0.4 to 1.0 ppm respectively (Kabata-Pendias and Pendias 1984). Bowen (1966) gave a typical background soil level of 0.1 ppm (Table 17). Background thallium values for surface muck (gley) soils have been reported at 0.20 and 0.22 ppm (Chattopadhyay and Jervis 1974). Samples of the muck soil from 0 to 7.5 cm and 22.5 to 30 cm depths exhibited thallium levels of 0.17 and 0.18 ppm respectively.

Little data are available on the effect of elevated thallium levels in soils and the resulting effect to plant production (Table 18). McCool (1933) has reported the injury to corn, ryegrass and wheat was not reduced by leaching soil with up to 91.5 cm (36 in) of water, but the extremely high concentrations of the Tl_2SO_4 (0.02 ml Tl_2SO_4/g soil) made these data of little use. Solution culture experiments by Potsch and Austenfeld (1985) and Pieper and Austenfeld (1985) have indicated concentrations of 10uM $TlNO_3$ or 10uM $Tl(NO_3)_3$ (10 uM = 2 ppm) produced significant reductions in the dry matter yields of pea plants but not in faba beans. Thallium levels up to 4.5 ppm have been reported in soils near an abandoned cement kiln plant (Scholl and Metzger 1981). These authors documented increased plant uptake of thallium from the polluted soils and noted thallium specific toxicity symptoms in some plants, but did not determine the effect on yield.

2.5.2 Thallium levels in plants

Few studies have investigated the toxicity of thallium to higher plants. The metal has not generally benefited from the large mass of data generated by sewage sludge disposal problems. Experimental data suggest that an increase in soil thallium levels increases uptake by plants (Hoffman et al. 1982, Scholl and Metzger 1981).

Experiments with barley roots suggested monovalent thallium was absorbed at a steady rate while trivalent thallium reached a plateau level in a short time (30 minutes in solution culture) (Logan et al. 1983). These authors found trivalent thallium was

Table 17. Background total thallium levels in soils.

Medium	Use	Level (ppm DW)	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Essen Soil	ND	0.1	Background	Plant Uptake	Vegetables	ND	Photometric	Field	Scholl and Metzger (1981)
Dautmergen	Crops	3.0	Background	Plant Uptake	Vegetables	Maturity	Photometric	Greenhouse	Hoffmann et al. (1982)
Ritzville Silt Loam	Soybeans	0.33	Background	Plant Uptake	Leaves, Stems, Pods	60 days	AAS	Soil Pots	Cataldo and Wildung (1978)
Scottland Topsoil	NR	0.17	Background	NR	NR	NR	SSMS	Field	Ure and Bacon (1978)
Scottland Topsoil	NR	0.37	Background	NR	NR	NR	SSMS	Field	Ure and Bacon (1978)
Canadian Muck Soil	Market Garden	0.21 (SUR)	Background	Plant Uptake	Garden Vegetables	NR	IPAA	Field	Chattopadhyay and Jervis (1974)
Canadian Muck Soil	"	0.17 (0-7.5 cm)	Background	Plant Uptake	"	NR	IPAA	Field	Chattopadhyay and Jervis (1974)
Canadian Muck Soil	"	0.18 (22.5-30.0 cm)	Background	Plant Uptake	"	NR	IPAA	Field	Chattopadhyay and Jervis (1974)

Table 13. Elevated total thallium levels in soils.

Medium	Use	Level (ppm DW)	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Dautmergen tL	Kohlrabi	503	24 % YR	Plant Uptake ($TlNO_3$)	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
"	Radish	503	51 % YR	"	Tubers	"	"	"	"
"	Radish	503	No YR	"	Leaves	"	"	"	"
"	Green Rapeseed	503	91 % YR	"	Tops	"	"	"	"
"	Lettuce	503	73 % YR	"	Leaves	"	"	"	"
Dautmergen tL	Kohlrabi	203	1 % Yield Increase	Plant Uptake ($TlNO_3$)	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
"	Radish	203	21 % YR	"	Tubers	"	"	"	"
"	Radish	203	8.7 % YR	"	Leaves	"	"	"	"
"	Green Rapeseed	203	38 % YR	"	Tops	"	"	"	"
"	Lettuce	203	62 % YR	"	Leaves	"	"	"	"
Dautmergen tL	Kohlrabi	53	12 % Yield Increase	Plant Uptake ($TlNO_3$)	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
"	Radish	53	39 % YR	"	Tubers	"	"	"	"
"	Radish	53	11 % YR	"	Leaves	"	"	"	"
"	Green Rapeseed	53	2.9 % YR	"	Tops	"	"	"	"
"	Lettuce	53	44 % YR	"	Leaves	"	"	"	"
Dautmergen tL	Kohlrabi	13	12 % Yield Increase	Plant Uptake ($TlNO_3$)	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffman et al. (1982)
"	Radish	13	10 % Yield Increase	"	Tubers	"	"	"	"
"	Radish	13	17 % YR	"	Leaves	"	"	"	"
"	Green Rapeseed	13	2.9 % YR	"	Tops	"	"	"	"
"	Lettuce	13	23 % YR	"	Leaves	"	"	"	"

readily desorbed by plants compared to monovalent thallium and concluded monovalent thallium was absorbed by plants in competition with potassium and therefore dependent on metabolic energy, whereas trivalent thallium was not. Monovalent thallium is apparently the most readily accumulated by plants due to its ionic radius which is similar to potassium and the element thus mimics potassium in many biological processes (Logan et al. 1983). Cataldo and Wildung (1978) demonstrated a 57 percent reduction of thallium uptake in the presence of a 10 fold increase in the potassium concentration. Thallium partitioning in plant parts is apparently very species specific. Work by Potsch and Austenfeld (1985) and Pieper and Austenfeld (1985) indicated that pea plants (Pisum sativum L.) concentrate thallium (as $TlNO_3$, $Tl(NO_3)_3$, Tl^{+1} EDTA and Tl^{+3} EDTA) in stems while field beans (Vicia faba L.) concentrate thallium in roots. These authors found thallium levels in pea leaves to be consistently higher than thallium levels in bean leaves in plants grown in the same concentration of thallium.

Background data for thallium levels in vegetation has been reported by several authors, including Geilmann et al. (1960) and Schacklette et al. (1978) (Table 19). Levels of thallium in plant tissues are generally much less than 1 ppm (Smith and Carson 1977a). However, values range from 0.008 ppm in clover to 35 ppm in kohlrabi.

Uptake of thallium by plants exposed to elevated thallium levels in soils follows the plant specific pattern. Green cabbage, which exhibits relatively higher background thallium levels (Geilman et al. 1961 and Hoffmann et al. 1982) also accumulates higher amounts under elevated conditions (Hoffman et al. 1982). Turnip leaves and rape plants can accumulate high levels of thallium (Hoffman et al. 1982). Scholl and Metzger (1981) demonstrated rape plants uptake 5 to 8 percent of applied thallium and 2 to 5 percent of natural soil thallium, and suggested the use of rape plants to decontaminate thallium polluted soils. These authors also noted green kale, turnips,

Table 19. Background thallium levels in plants.

Medium	Use	Level (ppm DW)	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Vegetation	Subalpine Fir	2-100 AWT	Background	Minimal	Needles	NR	NR	Rocky Mountains	Shacklette et al. (1978)
Vegetation	Subalpine Fir	2-70 AWT	Background	Minimal	Stems	NR	NR	Rocky Mountains	Shacklette et al. (1978)
Vegetation	Limber Pine	2-5 AWT	Background	Minimal	Needles	NR	NR	Rocky Mountains	Shacklette et al. (1978)
Vegetation	Limber Pine	3-5 AWT	Background	Minimal	Stems	NR	NR	Rocky Mountains	Shacklette et al. (1978)
Vegetation	Lodgepole Pine	2-5 AWT	Background	Minimal	Needles	NR	NR	Rocky Mountains	Shacklette et al. (1978)
Vegetation	Lodgepole Pine	3-7 AWT	Background	Minimal	Stems	NR	NR	Rocky Mountains	Shacklette et al. (1978)
Vegetation	Engelmann Spruce	2-10 AWT	Background	Minimal	Needles	NR	NR	Rocky Mountains	Shacklette et al. (1978)
Vegetation	Engelmann Spruce	15 AWT	Background	Minimal	Stems	NR	NR	Rocky Mountains	Shacklette et al. (1978)
Vegetation	Myrtle Blueberry	2-7 AWT	Background	Plant Uptake	Stems/Leaves	NR	NR	Rocky Mountains	Shacklette et al. (1978)
Vegetation	Ponderosa Pine	15 AWT	Background	Minimal	Stems	NR	NR	Rocky Mountains	Shacklette et al. (1978)
Vegetation	Clover	0.008-0.010	Background	Plant Uptake	NR	NR	NR	Field	Geilmann et al. (1961)
Vegetation	Meadow Hay	0.02-0.025	Background	Plant Uptake	NR	NR	NR	Field	Geilmann et al. (1961)
Vegetation	Head Lettuce	0.021	Background	Plant Uptake	NR	NR	NR	Field	Geilmann et al. (1961)
Vegetation	Red Cabbage	0.040	Background	Plant Uptake	NR	NR	NR	Field	Geilmann et al. (1961)
Vegetation	Green Cabbage	0.125	Background	Plant Uptake	NR	NR	NR	Field	Geilmann et al. (1961)
Vegetation	Leek	0.075	Background	Plant Uptake	NR	NR	NR	Field	Geilmann et al. (1961)
Vegetation	Endive	0.080	Background	Plant Uptake	NR	NR	NR	Field	Geilmann et al. (1961)
Vegetation	Beet	0.025-0.030	Background	Plant Uptake	Leaves	NR	NR	Field	Geilmann et al. (1961)
Vegetation	Potato	0.025-0.030	Background	Plant Uptake	Above Ground Biomass	NR	NR	Field	Geilmann et al. (1961)
Vegetation	Kohlrabi	35.	3.7 ppm Tl*	Plant Uptake	Leaves	NR	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Kohlrabi	0.10	3.7 ppm Tl*	Plant Uptake	Tubers	NR	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Zucchini	0.90	5.2 ppm Tl*	Plant Uptake	Leaves	NR	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Zucchini	0.02	5.2 ppm Tl*	Plant Uptake	Stems	NR	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Cucumbers	0.70	5.4 ppm Tl*	Plant Uptake	Leaves	NR	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Cucumbers	0.10	5.4 ppm Tl*	Plant Uptake	Fruit	NR	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Red Beet	2.40	5.2 ppm Tl*	Plant Uptake	Leaves	NR	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Red Beet	0.60	5.2 ppm Tl*	Plant Uptake	Tubers	NR	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Carrots	0.30	3.5 ppm Tl*	Plant Uptake	Leaves	NR	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Carrots	0.10	3.5 ppm Tl*	Plant Uptake	Roots	Nr	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Onions	0.10	0.9 ppm Tl*	Plant Uptake	Tops	NR	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Onions	0.01	0.9 ppm Tl*	Plant Uptake	Tubers	NR	Photometric	ND	Hoffmann et al. (1982)
Vegetation	Kohlrabi	30.0	3.0 ppm Tl*	Plant Uptake	Old Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Vegetation	Kohlrabi	6.0	3.0 ppm Tl*	Plant Uptake	Young Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Vegetation	Green Rapeseed	10.0	3.0 ppm Tl*	Plant Uptake	Tops	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Vegetation	Radish	1.1	3.0 ppm Tl*	Plant Uptake	Tubers	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Vegetation	Radish	4.5	3.0 ppm Tl*	Plant Uptake	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Vegetation	Lettuce	2.2	3.0 ppm Tl*	Plant Uptake	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)

* Soil

Table 20. Elevated thallium levels in plants.

Medium	Use	Level (ppm DW)	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Dautmergen Soil	Green Rapeseed	3326	91 % YR	$TlNO_3$	Tops	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Dautmergen Soil	Kohlrabi	2354	21 % YR	$TlNO_3$	Old Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Dautmergen Soil	Kohlrabi	1936	9.3 % YR	$TlNO_3$	Old Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Dautmergen Soil	Green Rapeseed	1656	38 % YR	$TlNO_3$	Tops	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Dautmergen Soil	Kohlrabi	1080	25 % YR	$TlNO_3$	Young Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Dautmergen Soil	Kohlrabi	1011	7 % YR	$TlNO_3$	Old Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Dautmergen Soil	Kohlrabi	591	7 % Yield Increase	$TlNO_3$	Young Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Dautmergen Soil	Green Rapeseed	499	2.9 % YR	$TlNO_3$	Tops	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Pea	440	56 % YR	Tl(I) EDTA	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Dautmergen Soil	Kohlrabi	382	7 % YR	$TlNO_3$	Old Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Pea	360	59 % YR	$TlNO_3$	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Dautmergen Soil	Radish	331	No Yr	$TlNO_3$	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Pea	320	47 % YR	Tl(III) EDTA	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Dautmergen Soil	Kohlrabi	299	24 % Yield Increase	$TlNO_3$	Young Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Pea	233	46 % YR	Tl(I) EDTA	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Sand Culture	Pea	230	41 % YR	Tl(III) EDTA	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Field Bean	222	18 % YR (N.S.)	$TlNO_3$	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Solution Culture	Pea	210	32 % YR (N.S.)	$TlNO_3$	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Solution Culture	Field Bean	200	8 % Yield Increase	Tl(III) EDTA	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Field Bean	180	5 % Yield Increase (N.S.)	Tl(I) EDTA	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Dautmergen Soil	Green Rapeseed	180	2.9 % YR	$TlNO_3$	Tops	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Dautmergen Soil	Radish	150	8.7 % YR	$TlNO_3$	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Pea	140	70 % YR	Tl(I) EDTA	Leaf	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Sand Culture	Field Bean	130	5.1 % YR	Tl(III) EDTA	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Pea	123	6.3 % YR (N.S.)	$Tl(NO_3)_3$	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Pea	120	69 % YR	Tl(III) EDTA	Leaf	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Dautmergen Soil	Kholrabi	116	24 % Yield Increase	$TlNO_3$	Young Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Pea	115	25 % YR	$Tl(NO_3)_3$	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Pea	110	60 % YR	Tl(I) EDTA	Leaf	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Sand Culture	Field Bean	108	11 % YR (N.S.)	$TlNO_3$	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Sand Culture	Field Bean	103	51 % YR	Tl(III) EDTA	Leaf	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Field Bean	88	15 % Yield Increase (N.S.)	Tl(I) EDTA	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Sand Culture	Pea	86	61 % YR	$TlNO_3$	Leaf	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Sand Culture	Corn	82	50 % Reduction Photosynthesis	Tl Salt	Leaf	4-5 days	AAS	Hydrophonic/Greenhouse	Carlson et al. (1985)
Sand Culture	Field Bean	76	11 % YR	$Tl(NO_3)_3$	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Pea	75	45 % YR	$TlNO_3$	Leaf	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Dautmergen Soil	Radish	64.4	11 % YR	$TlNO_3$	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Pea	63	6.7 % YR (N.S.)	Tl(III) EDTA	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Solution Culture	Sunflower	63	50 % Reduction Photosynthesis	Tl Salts	Leaf	4-5 days	AAS	Hydrophonic/Greenhouse	Bazzaz et al. (1974)
Sand Culture	Pea	58	30 % YR	Tl(I) EDTA	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Sand Culture	Pea	43	8 % YR (N.S.)	$Tl(NO_3)_3$	Leaf	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Field Bean	36	47 % YR	$Tl(NO_3)_3$	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Pea	36	17 % YR (N.S.)	$Tl(NO_3)_3$	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Pea	36	29 % YR (N.S.)	$TlNO_3$	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Dautmergen Soil	Radish	35.1	21 % YR	$TlNO_3$	Tubers	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Pea	35	31 % YR	Tl(III) EDTA	Leaf	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Dautmergen Soil	Lettuce	33	62 % YR	$TlNO_3$	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Dautmergen Soil	Radish	31.6	17 % YR	$TlNO_3$	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Dautmergen Soil	Radish	31.2	51 % YR	$TlNO_3$	Tubers	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Pea	30	37 % YR	$Tl(NO_3)_3$	Leaf	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Pea	30	32 % YR (N.S.)	$TlNO_3$	Leaf	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Sand Culture	Pea	29	21 % YR (N.S.)	Tl(I) EDTA	Leaf	ND	AAS	Geenhouse	Potsch and Austenfeld (1985)
Dautmergen Soil	Lettuce	28	44 % YR	$TlNO_3$	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Dautmergen Soil	Lettuce	25	73 % YR	$TlNO_3$	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Field Bean	25	2.3 % Yield Increase (N.S.)	Tl(III) EDTA	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)

Table 20. Elevated thallium levels in plants, continued.

Medium	Use	Level (ppm DW)	Hazard Response	Exposure Pathway	Receptor	Duration	Method	Study Setting	Reference
Sand Culture	Field Bean	23	13 % YR (N.S.)	$TlNO_3$	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Sand Culture	Barley	20 (11-45)	10 % YR	TlCl	Shoot	5 Leaf Stage	XRFL	Greenhouse	Davis et al. (1978)
Sand Culture	Pea	20	2.3 % YR (N.S.)	$Tl(NO_3)_3$	Leaf	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Dautmergen Soil	Lettuce	20	23 % YR	$TlNO_3$	Leaves	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Field Bean	19	14 % YR (N.S.)	$Tl(NO_3)_3$	Stem	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Dautmergen Soil	Radish	18.4	39 % YR	$TlNO_3$	Tubers	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Field Bean	16	4.6 % YR (N.S.)	Tl(I) EDTA	Stem	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Dautmergen Soil	Radish	8.6	10 % Yield Increase	$TlNO_3$	Tubers	Maturity	Photometric	Greenhouse/Soil Pots	Hoffmann et al. (1982)
Sand Culture	Field Bean	8	10 % YR (N.S.)	$TlNO_3$	Leaf	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Sand Culture	Field Bean	7	3.7 % YR	$Tl(NO_3)_3$	Leaf	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Field Bean	6	1.5 % YR (N.S.)	$TlNO_3$	Leaf	ND	AAS	Greenhouse	Potsch and Austenfeld (1985)
Sand Culture	Field Bean	5	39 % YR	$Tl(NO_3)_3$	Leaf	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)
Sand Culture	Field Bean	4	21 % Yield Increase	Tl(III) EDTA	Leaf	ND	AAS	Greenhouse	Pieper and Austenfeld (1985)

broccoli, kohlrabi and cabbage accumulated higher levels of thallium than most other vegetables.

Data for elevated thallium levels in plants are limited (Table 20). Up to 2.8 ppm thallium has been reported for plants near industrial sites (potash fertilizer works, smelter and bituminous coal plant) (Smith and Carson 1977a). Scholl and Metzger (1981) reported 22.6 ppm in green kale, 8.5 ppm in savory, 3.1 ppm in turnips, broccoli, kohlrabi and cabbage, and 0.5 ppm in radishes, carrots, onions, lettuce, tomatoes, cucumbers and numerous other vegetables; all grown on soil containing 4.5 ppm thallium. Hoffman et al. (1982) noted very high thallium levels in rapeseed plants and kohlrabi without large decreases in yields (Table 20). It is apparent that thallium uptake and toxicity are very species dependent and that the ability of some species to accumulate very high levels could pose a threat to the food chain. Hazard levels for thallium in soils and plants are presented in Section 3.5.

3.0 HAZARD LEVEL DEVELOPMENT FOR COPPER, MERCURY, SELENIUM, SILVER AND THALLIUM IN SOILS AND PLANTS

The selection of a phytotoxic level for a heavy metal in soil is complicated by the variance of the metal toxicity with soil characteristics and plant species. For example, the soil pH affects the availability of all five metals reviewed in this document. The availability of copper, mercury, silver and possibly thallium increases with decreasing pH. The availability of selenium increases with increasing pH. The pH of surface soils in the Helena Valley project area range from 4.7 to 8.2 with a mean of 7.2 (EPA 1986). The pH range of Helena Valley background surface soil sites is from 7.8 to 8.1. Most of the lower pH values found in the project area are confined to areas in or near the City of East Helena (EPA 1986).

The major complicating factor for the establishment of a critical hazard level in plant tissues is the wide variation observed among different plant species in metal uptake and their sensitivity to phytotoxicity. "It is clear that metal availability depends as much on the crop grown as on total and extractable concentrations of metal in soil" (Carlton-Smith and Davis 1983). The apparent critical toxicity of a given heavy metal in a specific tissue of a specific plant species appears to be relatively independent of different metal forms or the absorption process (Davis et al. 1978). Published phytotoxic levels for soils and plants are given in Tables 21 and 22, respectively. Table 23 presents values believed to be relevant to the Helena Valley study. The following sections describe how the values in Table 23 have been derived.

3.1 Copper Hazard Levels

Reported phytotoxic concentrations of total copper in soil range upward from typical background values (Table 2). A phytotoxic level of 100 ppm has been selected for the Helena Valley. All total soil copper concentrations in excess of 100 ppm, reported in the reviewed literature, were phytotoxic with yield reductions ranging from 14 to 28 percent. The 100 ppm

Table 21. Total concentrations of selected trace elements reported phytotoxically excessive in soils (ppm dry weight).

Notes	Ag	Cu	Hg	Se	Tl	Reference
		60				Kovalskiy and Andryomova (1968)
		100	5	10		El-Bassam and Tietjen (1977)
	2	100	0.3	5		Linzon (1978)
		100	2	10	1	Kloke (1979)
		125				Kitagishi and Yamane (1981)
26% Yield Reduction		200				Wallace et al. (1977a)
"Tolerable Margin"					1	Hoffman et al. (1982)
					4.5	Scholl and Metzger (1981)
Solution Culture Alfalfa		100 (mg/L)				Porter and Sheridan (1981)
Maximum Soil Limit for Sludge Application Recommended		50	2			Commission of the European Communities (1982)
Maximum Soil Limit for Sludge Application Mandatory		100				Commission of the European Communities (1982)
Maximum Permissible Levels in Sludges for use on Agricultural Lands		500-3000	5-25	14-100		Environmental Protection Services (1984)

Table 22. Plant tissue levels considered to be phytotoxic (ppm dry weight).

Notes	Ag	Cu	Hg	Se	Tl	Reference
5 Leaf Barley (Range)	4-5	18-21	2-5	7-90	11-45	Davis et al. (1978)
5 Leaf Barley (Mean)	4	20	3	30	20	Davis et al. (1978)
Maize Seedlings			6			Lipsey (1975)
		>20		50-100		Allaway (1968a)
		20				Reuther and Labanauskas (1966)
		20-30				Jones (1972)
		30				Leeper (1972)
5 Leaf Barley		20				Beckett and Davis (1977)
Oats (leaf)		28.8				Wallace et al. (1977a)
	5-10	20-100	1-3	5-30	20	Kabata-Pendias and Pendias (1984)
Rice Grain			0.5			Ishizuka and Tanaka (1962)
Bermudagrass (Fine Sand)-Toxic			6.4			Weaver et al. (1984)
		20				Ratsch (1974)
Bush Bean (stems)	5.1					Wallace et al. (1977d)
Bush Bean (leaves	5.8	29				Wallace et al. (1977d)
		20-40				Chaney et al. (1978)
Plantain Herbage/Clover Shoots		10-38				Dijkshoorn et al. (1979)
Rice Leaves		17-26				Chino (1981)
Orange Leaves		>23				Reuther et al. (1958)
Lemon Leaves		>20.0				Haas and Quayle (1935)
Oats (very chlorotic leaves)		37				Hunter and Vergnano (1953)
Snapbean Leaves		20-30				Walsh et al. (1972)
Peach Leaves (indicated as high range)		20-30				Kenworthy (1950)

Table 23. Proposed hazard levels for soils and plants in the Helena Valley study area.

Medium	Diagnostic Level	Site Location	Metal ppm DW				
			Copper	Mercury	Selenium	Silver	Thallium
Total Soil	Background	US[C]	24	0.09	0.3	0.70	0.02-2
Total Soil	Background	Helena Valley[D]	16.3	0.08	0.07	0.20	0.09
Total Soil	Background	This Report	1-300	0.005-1.97	0.005-5.1	0.01-5	0.1-3.0
Total Soil	Tolerable[A]		50	2	ND	ND	1
Total Soil	Phytotoxic[B]		100	5	10	2	10
Total Plant	Background	Global[C]	1-20	0.03-0.09	NR	NR	NR
Total Plant	Background	Helena Valley[E]	2.0	0.08	NR	0.4	NR
Total Plant	Background	This Report		0.001-0.237	0.001-84	0.06-1.4	
Total Plant	Tolerable		10	0.2	ND	2	ND
Total Plant	Phytotoxic		20	3	400	5	20

A. Tolerable refers to a soil or plant tissue element concentration that is greater than background, but scientific literature indicates this level has no adverse effect on plant biology.
B. Phytotoxic refers to a soil or plant tissue element concentration that will inhibit plant growth.
C. Kabata-Pendias and Pendias (1984).
D. Surface soil (0-4"), geometric mean, N=3 (EPA 1986).
E. Above ground biomass, average for alfalfa, cereal grains and grasses (EPA 1986).

phytotoxic total soil copper level has been suggested by several authors, including El-Bassan and Tietjen (1977), Linzon (1978), Kabata-Pendias (1979) and Kloke (1979). Baker (1974) reported phytotoxicity when soil levels exceed 150 to 400 ppm total copper and Kitagishi and Yamane (1981) have noted toxicity at soil levels of 125 ppm copper. The 100 ppm total soil copper concentration is the level at which McGrath et al. (1982) noted initial yield reductions in Lolium perenne (perennial ryegrass) when $CuSO_4$ was added to soil. No data have been found in the reviewed literature for phytotoxic total soil copper levels for alfalfa. Copper tolerant species may not be affected at the 100 ppm total soil copper level.

A tolerable level of 50 ppm total soil copper has been selected based on the reports of no yield loss to occasional small yield reductions noted below this level. This concentration is near the upper end of background levels found for many areas but below the 75 ppm concentration at which McGrath et al. (1982) noted decreased yields of Lolium perenne.

Total soil copper levels in the Helena Valley project area range from 10 to 41 ppm (EPA 1986). The geometric means for total soil copper in the project area and in the background site are 18.3 and 15.0 ppm respectively. Total soil copper levels present in the Helena Valley would not appear to be phytotoxic to crops.

Phytotoxic copper levels in plant tissues have been reported by numerous authors with good agreement. Phytotoxic values for leaves and shoots range from 15 ppm for plantain to 38 ppm for clover (Table 4). Similar values for barley shoots (Davis et al. 1978), rice leaves (Chino 1981), grass shoots (Dijkshoorn et al. 1979), oat leaves (Hunter and Vergnano 1953), and snap beans (Walsh et al. 1972) were 18 to 21 ppm, 17 to 26 ppm, 19 ppm, 37 ppm, and 20 to 30 ppm respectively. Copper levels found in clover were consistently higher than in grasses and copper was tolerated at higher tissue concentrations by clover as compared to grass (Kubota 1983, Dijkshoorn et al. 1979). Background legume tissue concentrations for various species were red clover (10.0 ppm) > alfalfa (8.8 ppm) > alsike clover (8.3 ppm) > sweetclover (7.9 ppm) = ladino clover (7.9 ppm) > lotus (7.4 ppm) (Kubota 1983). This author reported background copper values in grasses range from 5.9 ppm (smooth brome) to 4.0 ppm (wheat grass). Erdman et al. (1976) found copper levels consistently lower in grasses as opposed to corn and soybeans in several Missouri soils. These data suggest grasses in general will have lower tissue concentrations for a given soil copper level and apparently a lower phytotoxic tissue level.

A plant phytotoxic copper concentration of 20 ppm in leaf or shoot tissue would appear appropriate for the Helena Valley. This concentration may not produce phytotoxicity in alfalfa or other legume crops but is the level at which phytotoxicity may be expected to occur in most cereal crops, many grasses and some vegetables. A potentially useful tool for such an evaluation may be a system developed by Carlton-Smith and Davis (1983). This system presents ordered rankings (league tables) to compare the relative sensitivity of numerous crops to copper toxicity.

A determination of an overall tolerable level in plant tissues is difficult due to apparent differences in the sensitivity of various plant species. The problem is well exemplified by red clover and plantain. The 10.0 ppm background level for red clover (Kubota 1983) is the same level reported to result in a 50 percent yield reduction in plantain herbage (Dijkshoorn et al. 1979). The intermediate range (that level midway between copper deficiency and copper toxicity) values for a large number of fruits and crops commonly exceed 10 ppm with reported values for wheat and oat grain up to 16.7 ppm and 12.1 ppm copper respectively (Reuther and Labanauskas 1966). The level of 10 ppm suggested for East Helena will approximate a tolerable level for cereal grains. A tolerable level in a particular plant species may also be derived through use of a league table system.

3.2 Mercury Hazard Levels

The selection of a hazard level for mercury in soil can not be made with confidence with available data. Any hazard level for mercury should be specific for soil characteristics, mercury compound and plant species. This problem was demonstrated with the work of Weaver et al. (1984). These authors found the phytotoxic total mercury soil level varied from 8 to >50 ppm for bermuda grass, dependent upon the type of soil, with pH values (in the range of 4.7 to 7.7) apparently being insignificant. Levels considered to be phytotoxically excessive have been reported by several review publications (Table 21) and range from 0.3 to 5 ppm. The Environmental Protection Service (1984) gave a range of 5 to 25 ppm for the maximum total mercury content of sludges applied to agricultural lands.

A very tentative hazard level of 5 ppm total soil mercury is recommended for evaluating the Helena Valley data. This level is below that found by Weaver et al. (1984) to produce reduced plant growth in bermuda grass under their worst case condition. It is probable that levels considerably higher may be appropriate for soils high in clay or organic matter. Of the 160 surface soil samples analyzed from the Helena Valley, 5 samples exceeded 5.0 ppm total soil mercury (EPA 1986). All of these sites were within 0.81 km (0.5 mi) of the East Helena smelter complex. Total mercury levels for surface soil samples at Helena Valley background sites were within the range of typical background levels (Section 2.2.1). A tentative tolerable level of 2 ppm total soil mercury is suggested for the Helena Valley. This value is higher than the maximum background value of 0.78 ppm (Table 5). This level is well below the 8 ppm Weaver et al. (1984) found to be toxic to bermuda grass, but the 2 ppm tolerable concentration has little other support.

Phytotoxic hazard level for mercury in plant tissues are better defined than are those for soils. Davis et al. (1978) reported a phytotoxic level of 3 ppm for barley plants in the 5 leaf state using $HgCl_2$ in a sand culture. Yield reductions of 9.9 and 11 percent resulted in tomato plants with 0.6 to 0.8 ppm wet weight mercury levels in terminal (newest growth) foliage using methylmercury hydroxide (MMH) (Haney and Lipsey 1973). These authors found the dry matter content of the tomato plants varied between 8.4 and 11.9 percent of the wet weight, with a mean of 10.3 percent. Recalculating MMH concentrations on a dry weight basis indicates the observed yield reductions occurred at tissue mercury concentrations of 5.8 to 7.8 ppm. These values were quite similar to the 8 ppm mercury tissue concentration found to reduce yields of bermuda grass grown in $HgCl_2$ amended soil (Weaver et al. 1984). These limited data suggest that once absorbed and translocated to the above ground biomass, the phytotoxicity of the various mercury compounds may be similar. Phytotoxic plant tissue concentrations reported in the literature ranged from 0.5 ppm (for rice grain) to 6.4 ppm for bermuda grass foliage (Table 22).

The most appropriate hazard level for mercury in plants in the Helena Valley would appear to be the 3 ppm reported by Davis et al. (1978). This value fits well with the nontoxic mercury level of 2.9 ppm in bermuda grass reported by Weaver et al. (1984) and the 2.3 ppm level found to be nontoxic to alfalfa by Lindberg et al. (1979). A tolerable level of 0.2 ppm mercury in plant tissue is based upon the 0.2 ppm tissue level found to be toxic to bermuda grass under certain conditions (Weaver et al. 1984). Background concentrations near this level have been observed in onions and radishes (Table 7) but this level is 2 to 10 times higher than most observed background levels.

3.3 Selenium Hazard Level

The average background concentration of total soil selenium in the Helena Valley was reported to be 0.07 ppm (EPA 1986). This value is within the expected range of 0.005 to 4.0 ppm for total selenium in soils of the United States (Kabata-Pendias and Pendias 1984). Selenium is not known to retard plant growth at any concentration encountered naturally in soils, but toxicities to certain plants have been produced in a few greenhouse and field plot studies. Kabata-Pendias and Pendias (1984) reported that total soil selenium levels of 10 and sometimes 5 ppm were phytotoxically excessive. Hurd-Kauer (1934) found that a total soil selenium level of 30 ppm was toxic to wheat seedlings. A growth reduction of buckwheat resulted when total selenium concentrations in the soil ranged from 10.5 to 39.6 ppm (Martin 1936). These buckwheat plants died when soil selenium levels reached 76.6 ppm.

It must be noted that the various forms of selenium available for plant uptake have different degrees of toxicity (Trelease and Beath 1949). This and the limited and conflicting data regarding phytotoxic levels of selenium in soils pose difficulties in proposing hazard level. A tentative value of 10 ppm is suggested as the phytotoxic level for total soil selenium in surface soils of the Helena Valley. No data have been found in the reviewed literature concerning tolerable levels of soil selenium. An estimated value of 5 ppm has been determined intuitively by evaluating the toxic and background levels of selenium in soils of the United States, but no tolerable level for this parameter is recommended because of insufficient data. The total surface soil (0-4 inch) selenium value found for the Helena Valley background sites (n=3) is 0.07 ppm (Table 23). Similar values for the entire Helena Valley project area range from 0.07 to 1.30 ppm (EPA 1986).

Total selenium background levels for plant tissue from the United States range from 0.01 to 4.8 ppm (Connor and Shacklette 1975). While there are no reported cases of selenium being toxic to plants growing under natural conditions, there are a few cases of toxicity under experimental conditions. In the review by Kabata-Pendias and Pendias (1984), 5 to 30 ppm in mature leaf tissue was considered phytotoxic. The Environmental Protection Agency (1985) used 191 ppm in tomatoes and 429 ppm selenium in wheat as a toxic level when selenium was added to soil in sewage sludge application. A reduction of buckwheat plant growth occurred when tissue selenium levels ranged from 35 to 124 ppm. Death of these same plants occurred when tissue selenium levels reached 127 ppm (Martin 1936). Very low yields of alfalfa have occurred when the plant tops contained 360 ppm selenium and 1000 ppm is highly toxic (Soltanpour and Workman 1980). Yopp et al. (1974) reported no injury to wheat that contained 360 ppm total selenium.

The resistance to selenium toxicity ranges so widely among plants that a general toxicity level cannot be estimated with a high degree of confidence. The limited and conflicting data that are available compound this problem. A toxic level of 400 ppm total selenium in plants is recommended for the Helena Valley (Table 23). Only one source has been located that presented evidence of a tolerable level of selenium in vegetation (Yopp et al. 1974). The tolerable level of selenium in vegetation is be estimated at about 300 ppm but no level has been recommended because of insufficient data. Plant tissue selenium concentrations found in the Helena Valley project area range from 0.001 to 84 ppm (Table 23). These concentrations are below most concentrations that have been reported to be phytotoxic (Table 12).

3.4 Silver Hazard Levels

The background range of total surface soil silver in the Helena Valley was reported to be 0.09 to 0.45 ppm with a mean value of 0.20 ppm (EPA 1986). Total soil silver background levels for the entire nation seldom exceed 0.5 ppm (Connor and Shacklette 1975). No first hand research concerning phytotoxic levels of total silver in soils has been found in the reviewed literature. Kabata-Pendias and Pendias (1984) reported that 2.0 ppm total silver in soils was phytotoxically excessive. A tentative value of 2.0 ppm has been selected as the phytotoxic level for total soil silver in the Helena Valley based on this very limited information (Table 23). A tolerable concentration for total soil silver is likely about 1.0 ppm, but this value has little support from the reviewed literature. Total surface soil silver concentrations found for the Helena Valley project area ranged from 0.09 to 46 ppm (EPA 1986).

Background silver concentrations in plant tissue generally range from 0 to 1.0 ppm with most concentrations below the 0.25

ppm level (Table 15). Background silver concentrations in vegetation reported for the Helena Valley ranged from 0.35 to 1.0 ppm (EPA 1986). Data pertinent to the toxicity of silver in plants are also extremely limited. The review by Kabata-Pendias and Pendias (1984) indicated 5 to 10 ppm silver in plant tissue was excessive or toxic. The yield of bush beans was greatly decreased at stem and leaf silver concentrations of 5.1 and 5.8 ppm respectively (Wallace et al. 1977d). No effect in bush bean yield has been noted with stem and leaf tissue levels of 0.8 and 1.0 ppm silver, respectively. Davis et al. (1978) reported that a 10% yield reduction occurred in spring barley with 4.0 ppm silver in the plant tops. With this limited data, a tentative value of 5.0 ppm silver in plant tissue is suggested as the phytotoxic level (Table 23). A tolerable plant tissue silver concentration of 2 ppm is suggested for the Helena Valley based on background levels and limited experimental data.

3.5 Thallium Hazard Levels

Background total soil thallium levels in North America are generally less than 0.5 ppm (Table 17), and typical background total soil thallium concentrations range from 0.02 to 2 ppm (Kabata-Pendias and Pendias 1984). The background surface soil concentration reported for the Helena Valley was 0.09 (EPA 1986). Thallium levels at which phytotoxic symptoms have been noted range from 1 umol/l (.2 ppm) for corn and sunflowers in solution culture to 1.4 ppm in soil noted by McCool (1933) for damaged wheat plants. McCool (1933) reported wheat plants were killed at a soil thallium level of 28 ppm. Carson and Smith (1977) state "many crop plants are injured by concentrations of about 7 ppm in the soil," and noted toxic effects to tobacco plants at 1 ppm thallium in soil and 0.4 ppm thallium in water. Cataldo and Wildung (1978) found 40 percent of 2.5 ug/l thallium applied to soil was still in soluble form after 13 days. Similar values for arsenic, cadmium, lead and zinc were 8.8, 34, <1, and 8.2 percent respectively. This study suggests that thallium may be proportionately more available to plants than most soil metals. It is difficult to determine a specific hazard level for thallium in soil due to the wide variation in tolerance and uptake exhibited by various species of plants and due to the scarceness of data. Hoffman et al. (1982) experienced mixed results with total soil thallium levels from 13 to 503 ppm (Table 18). Scholl and Metzger (1981) noted specific toxicity symptoms in some crops grown on a polluted soil containing 4.5 ppm. Total surface soil thallium values reported for the Helena Valley project area ranged from 0.09 to 2.40 ppm (EPA 1986).

A phytotoxic level for total soil thallium of 10 ppm is suggested for the Helena Valley, but has only marginal support from the reviewed literature (Table 23). Scholl and Metzger reported some toxicity symptoms at total soil levels of 4.5 ppm thallium and Hoffman et al. (1982) reported a 23 percent reduction in the yield of lettuce at 13 ppm total soil thallium. The 10 ppm hazard level should be considered very tentative until research provides more information. Hoffman et al. (1982) suggested 1.0 ppm total soil thallium as a "tolerable margin" and, in the absence of contradicting data, this concentration is suggested as the tolerable level for the Helena Valley.

Hydroponic culture experiments with peas and faba beans utilizing thallium^{+1} and thallium^{+3} (as $TlNO_3$, Tl^{+1} EDTA, $Tl(NO_3)_3$ and Tl^{+3} EDTA) suggest significant yield decreases in peas will occur at leaf thallium levels near 30 ppm for $Tl(NO_3)_3$ (Pieper and Austenfeld 1985, Potsch and Austenfeld 1985). These studies indicate $TlNO_3$ is less toxic in plant tissue at comparable concentrations than $Tl(NO_3)_3$. Pea leaf levels of 75 ppm thallium as $TlNO_3$ were required to produce similar yield reductions experienced with 30 ppm thallium leaf levels using $Tl(NO_3)_3$. Faba beans were apparently highly resistant to thallium toxicity up to the 2.04 ppm used in the hydroponic solution. The maximum faba bean leaf thallium content (8 ppm), using 2.04 ppm thallium as $TlNO_3$ in the hydroponic solution, did not produce significant yield reductions (Potsch and Austenfeld 1985). Thallium concentrations up to 27 ppm have been observed in some of the 35 garden species grown in thallium contaminated soil (Scholl and Metzger 1981). These authors have indicated that some thallium specific symptoms occurred in some species, but no decrease in yields were apparent. Carlson et al. (1975) found a 50 percent reduction in photosynthesis in corn and sunflowers at leaf concentrations of 82 ppm thallium and Bazzaz et al. (1974) have noted a 50 percent reduction in sunflower leaf photosynthesis at a tissue concentration of 63 ppm. Davis et al. (1978) found 11 to 45 ppm thallium in the leaves of 5 leaf stage barely seedling to be toxic and have reported 20 ppm in barley leaf tissue as the "upper critical level" associated with a 10 percent yield reduction in this species. Based on the limited data available, the 20 ppm thallium tissue concentration has been selected as the phytotoxic level for the Helena Valley (Table 23).

A tolerable thallium concentration in plant materials has not been recommended but is likely less than the 5 ppm in leaf tissue that Pieper and Austenfeld (1985) found to produce a 39 percent yield reduction in faba beans. More research is needed to properly define a tolerable thallium level for plants especially for crops typical of the Helena Valley.

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